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Method for Analyzing Emissions from Atmospheric Fluidized-Bed Combustor

Battelle Columbus Labs, Ohio

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Industrial Environmental Research Lab, Research Triangle Park, N C

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METHOD FOR ANALYZING EMISSIONS FROM ATMOSPHERIC FLUIDIZED-BED COMBUSTOR

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Program Report

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ABSTRACT

A methodology for comprehensive sampling and analysis of emissions from an atmospheric fluidized-bed combustor has been developed and tested experimentally. The methodology tested is a first attempt to develop an approach to the Level 1 methodology as defined by TRW and is aimed at providing a cost and information effective environmental assessment of fluidized-bed combustion (FBC) units. Included in the report is a general discussion of the pertinent areas likely to be encountered in sampling and analysing specimens from FBC units, as for example, the streams encountered in FBC units, the selection of streams, procedures for sampling the gaseous, solid, and liquid streams, and the multi-level analysis approach to characterisation of emissions from combustion units as defined by EPA.

The adopted experimental methodology was put into practice, using Battelle's 6-inch atmospheric FBC unit. The details involved in sampling and analysing the samples from the 6-inch FBC unit are discussed in relation to (1) the preparatory work, i.e., background information, site survey, development of a sampling and analysis plan, installation of equipment, and shake down runs, (2) sampling procedures involved with the FBC unit, and (3) analysing the samples taken from the FBC unit. The analytical data obtained from two runs made with the unit are presented and discussed, mainly in terms of the trace element data obtained. These data and other pertinent gaseous and particulate data are compared to data obtained from other FBC and/or conventional fired units. The report concludes with the presentation of a generalized sampling and analysis plan to be used as a guide in characterising the emissions from FBC units.

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SECTION 1

INTRODUCTION AND OBJECTIVES

Fluidized-bed combustion (FBC) offers specific advantages over other coal-fired combustion processes in that it provides high thermal efficiency and capability for in-situ antipollution control. Total environmental assessments of FBC processes are only now being initiated, thus comprehensive procedures for collecting and analysing FBC emission products as well as reactant products are needed. The objective of this program was to develop and test primarily a Level 1 methodology* for comprehensive analysis of emissions from an atmospheric FBC unit and to consider the application to pressurized fluidized-bed combustors as well as to other coal-burning processes.

This report summarizes a program carried out under Task 33, EPA Contract No. 68-02-1409. The emphasis in this program was mainly on establishing a general methodology for comprehensive sampling-analysis from FBC units and not to define the precision and/or accuracy of the techniques employed. To achieve the overall objective of the program, four distinct phases were considered. These were:

A. Developing a preliminary approach for comprehensive analysis
B. Designing and conducting a test program
C. Evaluating the emission data
D. Refining the preliminary comprehensive analysis approach.

Along with developing the general methodology, the development was tested using Battelle's 6-inch fluidized-bed combustor.

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* Level 1 methodology similar to that defined by TRW (1); all references are on page 49.

SECTION 2

PRELIMINARY PLAN DEVELOPMENT

At the time this program was undertaken two pertinent activities were in progress. MITRE Corporation (2) was completing a state-of-the-art survey of fluidized-bed sampling and analysis procedures and was developing guidelines for carrying out these procedures, and IERL/RTP (3) was in process of formalizing the Level 1-2-3 sampling-analysis concepts. Both of these programs impacted on this program and provided useful background information. Pertinent information in these program is reviewed here.

TECHNICAL BACKGROUND - REVIEW OF SAMPLING ANALYSIS PROCEDURES AND CONCEPTS

The MITRE report* is pertinent to this sampling program in that it presents a detailed up-to-date study of the tentative procedures for environmental assessment of fluidized-bed units. The primary objective of the work covered in the MITRE report was to develop sampling and analysis procedures for use by source contractors in support of the environmental assessment of fluidized-bed combustion technology. The review presented here covers briefly the areas of interest to this program, i.e., sampling and analyses procedures and concepts, and constituents likely to be encountered in fluidized-bed sampling. Pertinent information from a Battelle planning study report (4) is included in the review.

Selection of Influent and Effluent Streams

In order to characterize the emissions from combustion processes, it is important to consider all possible streams in the combustion system which may lead to pollutant formation. In the case of the FBC units, a total of 30 different streams have been recognized as possible sources of pollutants. The 30 streams are shown in Table 1. The relationship of the various streams to a generalized FBC system is shown in Figure 1.

* The review covered in this report is from the First Draft of the MITRE report. A Second Draft of the report has been completed and some changes are likely to have been made.

TABLE 1. STREAM IDENTIFICATION FOR GENERALIZED FBC SYSTEM

Stream No.	Stream Identification
1	Stack Gas from FBC
2	Particulate Removal Discard from FBC
3	Bed Solids Discard from FBC
4	Particulate Removal Discard--Regeneration Operations
5	Other Effluents from Regeneration and Sulfur Recovery Operations
8	Product from Sulfur Recovery (Sulfur or Sulfuric Acid)
9	Fugitives from Fuel Preparation
10	Fugitives from Sorbent/Additive Preparation
11	Raw Fuel to Preparation
12	Raw Sorbent/Additive to Preparation
14	Air to Combustor
15	Air/Steam to Regenerator
16	Fuel Feed to FBC
17	Fuel Feed to Regenerator
18	Start-Up Fuel Feed to FBC
19	Prepared Sorbent/Additive Feed to FBC
20	Bed Solids to Regenerator
21	Flue Gas from FBC to Particulate Removal
23	Recycle of Particulates from Particulate Removal to FBC
24	Recycle of sorbent from Regeneration
31	Fugitive or secondary Emission from Fuel Storage Facility
32	Fugitive or Secondary Emission from FBC Discard Bed Material
33	Fugitive or Secondary Emission from FBC Particulate Disposal
34	Effluent Gas from Secondary Stack Gas Cleaning Device (Similar to Streams 25 & 26 in MITRE Study)
35	Discard from FBC Secondary Stack Gas Cleaning Device
36	Flue Gas from Regenerator to Particulate Removal
37	Fugitive or Secondary emission from Regeneration Bed Discard
38	Stack Gas from Regenerator to Sulfur Recovery Operations
39	Fugitive or Secondary Emissions from Regenerator Particulate Disposal
40	Fugitive or Secondary Emissions from Sorbent Storage Facility

Figure 1. [illegible]

The numbering system has been adopted from MITRE.[2]

Many of the streams listed in the table are encountered in combustion processes other than FBC units and would be considered there as appropriate. On the other hand, some streams encountered in some FBC units have been intentionally omitted from Table 1 on the basis of their low priority, or because they apply to units which were judged inappropriate for inclusion in this study program, e.g., the CAFB units.

For each FBC unit sampled, certain criteria should be considered before selecting or rejecting a sample stream. Overall, stream characterization should be made when:

- A direct emission stream is representative of a FBC process release to the environment
- A feed or supply stream will significantly affect direct emissions
- A within-process stream might significantly affect an emission stream or the performance of an emission control device
- A fugitive emission is identified, or suspected, which might be characteristic of a reduced-to-practice FBC unit
- A secondary emission is simulated in a supplementary test involving a supply or effluent stream.

Sampling Procedures for Solid, Liquid, and Gaseous Streams

Many of the selected streams will require special sampling techniques. The following discussion is a synopsis of the recommended techniques to be used in sampling solid, liquid, and gaseous streams, as well as suggestions for sampling fugitive emissions. These are presently the tentative recommended procedures.

Solid Streams--

Recommended techniques for sampling solid streams include:

- Grab-full stream cut
- ASTM pulverized coal samples
- Automatic-full stream cut-Vezin type samples
- Stopped belt sampling method.

In using these techniques, one should also take into consideration,

1. Heterogeneous nature of the material and degree of stratification likely to be encountered

2. Tendency of different size fractions to concentrate certain materials in sample, e.g., some trace elements may tend to concentrate in the smaller size fractions.

With the above two points in mind, it would appear that the full stream cut or the stopped belt methods would provide the best representative samples from solids.

The following considerations should also be observed in sampling solid streams to minimize contamination of the sample.

1. Sampling equipment surfaces in contact with sample should be made of stainless steel to minimize erosion effects.

2. Sample container material should have weak erosive potential and be acid resistant and free of toxicological contaminant. Kapton is generally acceptable.

3. Air-tight stainless steel containers should be used for high temperature samples.

Liquid Streams--

The recommended procedures for sampling liquid streams include:

- Grab-full stream cut
- Tap
- Automatic high volume samples
- Carbon absorber concentration techniques.

Sampling liquid streams is relatively straightforward if there are no suspended particles or non-miscible liquids in the stream. Since this is not generally the case, representative sampling of liquids becomes more difficult. Point sampling and high non-isokinetic flow rate sampling are the prevalent methods in water sampling. These techniques can be considered accurate for most needs but may not suffice for trace sampling. Further work is needed to verify the sampling techniques in this area.

In sampling liquids for trace metals, the liquid is filtered on site and the filtrate stabilized with nitric acid. For trace organics, no filtering is involved; the sample is preserved by refrigeration at 4° C. In sampling liquid systems, Teflon, stainless steel and glass are the only materials usually used.

Suspended Particulate--

The Source Assessment Sampling System (SASS) train is the recommended technique (5) for suspended particulate sampling of fluidized-bed units. This unit and the Method 5 train fulfill the following criteria necessary for efficient particulate sampling:

1. Provide sufficient quantity of sample for analyses at each particle-size fraction desired.
2. Minimize number of sampling trains and avoid excessive personnel interference.
3. Meet precision and accuracy goals defined for each sampling level (Level 1 and Level 2 discussed later).

The SASS train meets all the above criteria for Level 1 particulate sampling and criteria 1 and 2 for Level 2 sampling. The Method 5 rig with an impactor and a high volume cyclone train meets criteria 3 for Level 2 particulate sampling, and in some cases may meet criteria 1.

The following considerations are important in particulate sampling for minimizing contamination of either the trace organic, trace inorganic measurements, or bioassay procedures.

- Stainless steel 316 should be maintained as the principal material of construction with Viton-A used as gasket materials.
- Filters should be high-purity quartz material and should be routinely analyzed to insure low inorganic concentration.
- Trains must be packed and unpacked in a clean room environment to minimize contamination.

Gases--

The recommended techniques for sampling of gaseous components include:

- EPA Methods 3 through 7 (6), and 10 (7)
- ASTM methods
- Absorbing solution methods
- Condensation methods and others.

All of the chosen techniques have had proven field experience, except for the porous polymer adsorber technique for nonvolatile hydrocarbons. Options to some of the selected methods are available and are presented in the Mitre report.

Other considerations in sampling gases are

1. Organic grab samples taken in glass bombs should not be left in sunlight and should be analyzed as soon as possible.

2. Precautions must be taken to insure no stratification of sample occurs.

3. Materials of construction must be inert towards the sample material.

Fugitive Emissions--

Fugitive emission measurements are made on the basis of a background versus operating plant method. Background ambient air quality measurements are documented prior to the plant's construction or during a plant shutdown for those plants already constructed. In the latter case, the aggregated storage piles would have to be covered during the background measurements. The background measurements are compared to measurements made during plant operation and fugitive emission levels determined from the two measured levels. A meteorologist should determine the duration of background and operation fugitive testing.

Sampling and Analysis Strategy

A multilevel approach is used in sampling and analysing samples from the various selected streams of a combustion process. The levels are referred to as Level 1, 2, and 3. Each of the levels is defined below, as taken verbatim from reference (3). A more detailed report covering Level 1 sampling and analyses has been issued recently by EPA (5). Level 2 procedures are currently being worked out. Level 3 will require further considerations.

Level 1 Sampling--

"Level 1 sampling stresses the concept of completeness by presuming that all streams leaving the process will be sampled unless empirical data equivalent to Level 1 outputs already exist. Further, Level 1 sampling is not predicated on a priori judgements as to the composition of streams. The techniques prescribed presume that whatever prior knowledge is available is at best incomplete. Predictive and extrapolation techniques employed during environmental assessments serve as a check on the empirical data and not as a replacement for it.

Level 1 sampling programs are therefore envisioned to permit detection of the presence of all substances in the stream. They do not necessarily produce information as to specific substances or their chemical form. For example, if sulfur-containing gases are in the gas stream, Level 1 sampling will trap and retain the sulfur. However, it is not designed to preserve the sulfur con-

pounds as H_2S, SO_2, COS, C_4H_4S, $(CH_3)_2S$, etc. (In many cases a reasonably specific compound identification may result at Level 1, but conceptually it is not necessary in judging the success of Level 1.)

Level 1 sampling programs are designed to make maximum use of existing samples and stream access sites. While some care must be exercised to ensure that the samples are not biased, the commonly applied concepts of multiple-point, isokinetic or flow proportional sampling are not rigidly adhered to. Normally, a single sample of each stream should be collected under average process operating conditions, or alternatively, under each condition of interest. These samples should be time-integrated over one or more process cycles. When a series of discrete samples results, they are combined to produce a single "average" for analysis.

Level 2 Sampling--

Level 2 sampling programs are directed towards a more detailed characterization of stream composition. They are not as "complete" as Level 1 in that resources are expended to improve information on streams of a critical nature. Additional sampling of other streams may be deferred because Level 1 information has indicated a potentially less-significant level of environmental impact. Level 2 sampling is optimized for specific compounds or classes of compounds contained in the streams sampled. It also provides a more quantitative description of the concentrations and mass flow rates of the various substances in the stream.

Level 2 sampling is considerably more refined than Level 1, since it is being conducted on streams that have already been identified as having potentially adverse environmental effects. In some instances, Level 2 will use the same sampling techniques and equipment as Level 1. The primary difference will be a more rigorous attention to selection and preparation of sampling sites and adherence to procedures for acquiring a representative sample. Level 2 sampling should also provide for replication of samples in order to further improve on accuracy and representativeness.

In many cases, Level 2 sampling will utilize modifications of Level 1 techniques and/or the application of entirely new methods. Such cases result from the necessity to identify more definitively the materials which produce the adverse environmental problems. For example, if Level 1 has indicated a

high concentration of sulfur-containing species, Level 2 sampling must be specifically designed to provide isolation of the materials into appropriate forms for subsequent analysis.

Level 3 Sampling--

At Level 3, emphasis is placed on the variability of stream composition with time and process or control system parameters to define accurately the range of values to be expected. An effective Level 3 sampling program is designed to monitor a limited number of selected compounds or compound classes.

Level 3 sampling is designed to provide information over a long period of time. To be cost effective, such programs must be tailored to the specific requirements of each stream being monitored. Based on the information developed at Level 2, specialized sampling procedures can be designed to track key "indicator" materials at frequent intervals. Level 3 should also incorporate continuous monitors if at all possible.

During Level 3 programs, it is anticipated that more complete Level 2 type sampling will be conducted at predetermined intervals to check the limited Level 3 information. Further, recommended procedures for compliance testing should be introduced into the program at a time appropriate to the status of process or control technology development."

Table 2 characterizes the Level 1-Level 3 strategy for combustion sampling. Although the extent of the Level 2 and Level 3 sampling will depend on results from Level 1 and Level 2 sampling, respectively, it is likely that hybrids of these levels will be used in most combustion sampling programs. As seen later in this report the present sampling program used a combined Level 1-Level 2 approach. The extent to which this occurs depends largely on the information desired and the relative cost incurred in obtaining the extra data.

Sample Preservation and Handling*

Avoidance of contamination and degradation of samples is of prime importance in the comprehensive analysis of FBC units. Contamination considerations extend from the preparative and packing stages, through the various collection procedures, and to the analysis of the collected samples.

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* Discussion taken from reference 4, page 33.

TABLE 2. GENERAL CHARACTERISTICS OF PHASED LEVEL 1-LEVEL 2 STRATEGY (2)

Issue	Level 1	Level 2
GENERAL		
• Goal	Detection of potential pollutants and planning basis for Level 2	Accurate measurement of specific pollutants and determination of mass emission rates
• Process operating conditions	Steady-state representative condition	Steady-state representative condition
• Streams considered	All system influents and effluents	Selected system influents and effluents
• Pollutant classes/species addressed	All pollutant classes	Selected class/species
SAMPLING CHARACTERISTICS		
• Representative of sample	Sufficient for detection of all potential pollutants	Consistent with Level 2 goals
• Sampling technique	Particulates: initially isokinetic, single point Gases: single point grab unless stratification exists (when full traversed) Solids and liquids: partial stream cut	Particulates: isokinetic, full traverse (gases: single point unless stratification exists (when full traversed); construction of integrated grab; use Federal Register methods; and continuous on-line samples Solids and liquids: full stream cut (minimum requirement)
• Sampling location	Level 2 sampling locations (as incorporated into generic plant design) used for Level 1 sampling where practical Particulates: cross-section point of average velocity Gases: same location as for particulates Solids and liquids: most convenient location consistent with obtaining partial stream cut	Recommend Level 2 sampling capability be incorporated in generic plant design Particulates: full traverse of cross-section; distances from disturbances sufficient to minimize irregular flow patterns Gases: same location as for particulates Solids and liquids: most convenient location consistent with obtaining full stream cut
• Replications	Particulates: 3 minimum; composite for sample and analysis Gases, solids, liquids: none	Particulates: 3 minimum; separate analysis for each sampling Gases: compliance with Federal Register specs; statistically designed to relate manual with continuous on-line
• Sample quantity	Gases and particulates: dictated by analytical method employed Solids and liquids: per ASTM method	Gases and particulates: dictated by analytical method employed Solids and liquids: per ASTM method and Federal Register specs
ANALYTICAL CHARACTERISTICS		
• Sensitivity	Highest sensitivity (consistent with Level 1 resources)	Sensitivity requirements dictated by Level 1 output
• Accuracy	Order of magnitude	High accuracy
• Replication	None planned	Statistically designed
• Specificity	Broad classes of organics Some species (inorganic and organic)	Individual species corresponding to class/species identified at Level 1
• Gas analysis	Gas chromatography; absorption tubes	Primary reliance on GC (or best method for individual species)
• Elemental analysis	Spark source mass spectrometry	Atomic absorption spectroscopy (or best method for individual species)
• Anion analysis	Not performed	Method dependent on individual species
• Organic solids and liquids	Extraction, separation into functional classes Analysis by fourier transform infrared spectroscopy	Extraction, separation by high resolution liquid chromatography Analysis by GC/Mass spectroscopy, IR, NMR (or best method for individual species)
BIOASSAY CHARACTERISTICS		
• Analyses performed	Cytotoxicity, mutagenicity	Cytotoxicity, mutagenicity, carcinogenicity

Containers used for packaging reagents for field use and storage of samples should be dedicated to this purpose and scrupulously cleaned before put in storage for subsequent use.

The collection and packaging of samples to be used for carcinogenicity and mutagenicity should be handled in such a way as to minimize the amount of degradation brought about by air, temperature, and light. Ideally, the collected samples should be placed in brown bottles, purged with nitrogen or argon, sealed, and frozen in dry ice. Brown bottles are often difficult to obtain and cylinders of inert gas are frequently not available for field use. When these adverse conditions prevail, the sample collection protocol would be altered to use clear wide mouth jars or bottles. Immediately following the collection of the sample, the container is sealed with tape around the lip of the lid and wrapped in aluminum foil. Once sealed, the containers should be carefully packed in dry ice of sufficient quantity to ensure arrival of the frozen samples at their destination. Refrigeration at temperatures near freezing or below is the best preservation technique available, but is not applicable to all types of samples. Samples in water solutions cannot be frozen in glass bottles due to possible breakage. At best, preservation techniques can only retard the chemical and biological changes that inevitably continue after the sample is removed from the parent source. Contamination and degradation of samples can best be avoided by analyzing the samples as soon as possible after collection.

Quality Control in the Sampling Program*

Quality control must be supplied in the sampling program to assure that representative samples are obtained from the various process streams and that the sample integrity is not compromised prior to delivery to the analytical laboratory. Obtaining representative samples requires that appropriate sampling locations and sampling technique be selected. These factors will be especially critical when sampling the stack and flue gas streams for particulates. Maintenance and calibration of equipment is also essential to collection of representative samples. Calibration of flow meters and temperature measuring devices should be performed before each field trip. Pitot

* Discussion taken from reference 4, page 35.

tubes should be calibrated and leak tests made on the sampling trains on a regular basis. Checks should be performed in the field to verify the equipment is still within calibration. Spares should be available to replace defective equipment.

Maintaining sample integrity demands that careful consideration be given to materials used in the sampling systems or equipment. Materials should be chosen to minimize the introduction of contaminants. Sample recovery from particulate sampling trains must be performed in an area and using equipment and techniques which will not contaminate the samples. All samples must be stored in containers which are leak-tight and which do not introduce contamination. Certain samples (for organic analyses and bioassays) must be protected from light and temperature extremes to maintain the integrity.

Continuous gas monitoring instrumentation presents special calibration requirements. During a field program, these instruments should be calibrated before and after each test using standard gas mixtures. Periodic analyses should be performed to verify the concentrations of these calibration (span) gases stated by the gas suppliers.

SECTION 3

METHODOLOGY DEVELOPMENT

In consideration of the preceding discussions, the methodology development in the present program was based around sampling and analysis experiments with Battelle's 6-in. fluidized-bed unit. The Battelle unit provided a means for evaluating the generality of proposed procedures in the laboratory.

DEVELOPMENT OF A COMPREHENSIVE SAMPLING AND ANALYSIS PLAN

A considerable amount of planning and preparation was required prior to carrying out the sampling and analysis plan for the 6-inch FBC unit. The preliminaries include, appropriate background information on the unit, development of a sampling and analysis plan for the unit, site survey and planning, installing and operating equipment, and shake down runs.

Background Information

Prior to the actual sampling of a FBC unit, it is essential that the appropriate personnel become throughly familiar with the design and general operation of the unit. Pertinent areas of interest include but are not limited to

- Process description
- Process schematic flow sheets
- Plant layout
- Equipment specification
- Plant personnel data
- General range of firing conditions capable with the FBC
- Results of any previous emission testing.

Background information relating to the design and general operating features of the Battelle unit is discussed below.

Battelle 6-in. FBC--

The 6-in. FBC facility at Battelle can be fired in different velocity modes with solid fuels at rates up to 50 lb/hr. Preheaters enable the incoming gases to be heated to nearly 1000 F, as desired, prior to combustion. Fluidized-bed operating temperatures from 1400 to 1800 F are established through control of the fuel feed-rate and preheat temperatures.

Figure 2 shows a scaled drawing of the 6-in. FBC unit used in this program. Figure 3 is a photograph of the unit. For this work, it was desirable to fire the combustor in a low velocity mode typical of that used in conventional FBC units. High sulfur Illinois Number 6 coal was used for the fuel and grove limestone served as the bed material. These are fed to the combustion chamber on a small conveyer belt. Cyclones are used in the flue gas and sampling streams to fractionate particle sizes. Normally, two cyclones are present in the flue gas stream from the FBC unit, but for this sampling program, only one cyclone was used in this stack gas region. This cyclone (No. 1) removes all particulates above about 37 microns. A second smaller cyclone was installed in the Method 5 rigs to remove particulates between about 37 and 3.3 microns in the sampled gas. This is discussed later.

Sampling ports are available at several different points in the combustor. These are indicated in Figure 2 by the capital letters A, B, C, D, and E. The legend in the figure describes the general type sampling taking place at each port. An overflow tube (T) inside the bed reaction chamber maintains the height of the bed at 4-ft and allows continuous removal of the bed materials during a run. The overflow tube acts essentially as a sampling port within the fluidized-bed region.

The flue gas, after passing the final sampling Port C, is directed into a water scrubber where the gases are further cleaned before exiting to the atmosphere. Solid material (sludge collected in the scrubber) is removed from the scrubber by filtering.

The above background information provided a basis for choosing sampling locations, proper sampling conditions, and selection of appropriate sampling streams with subsequent development of a sampling and analysis plan.

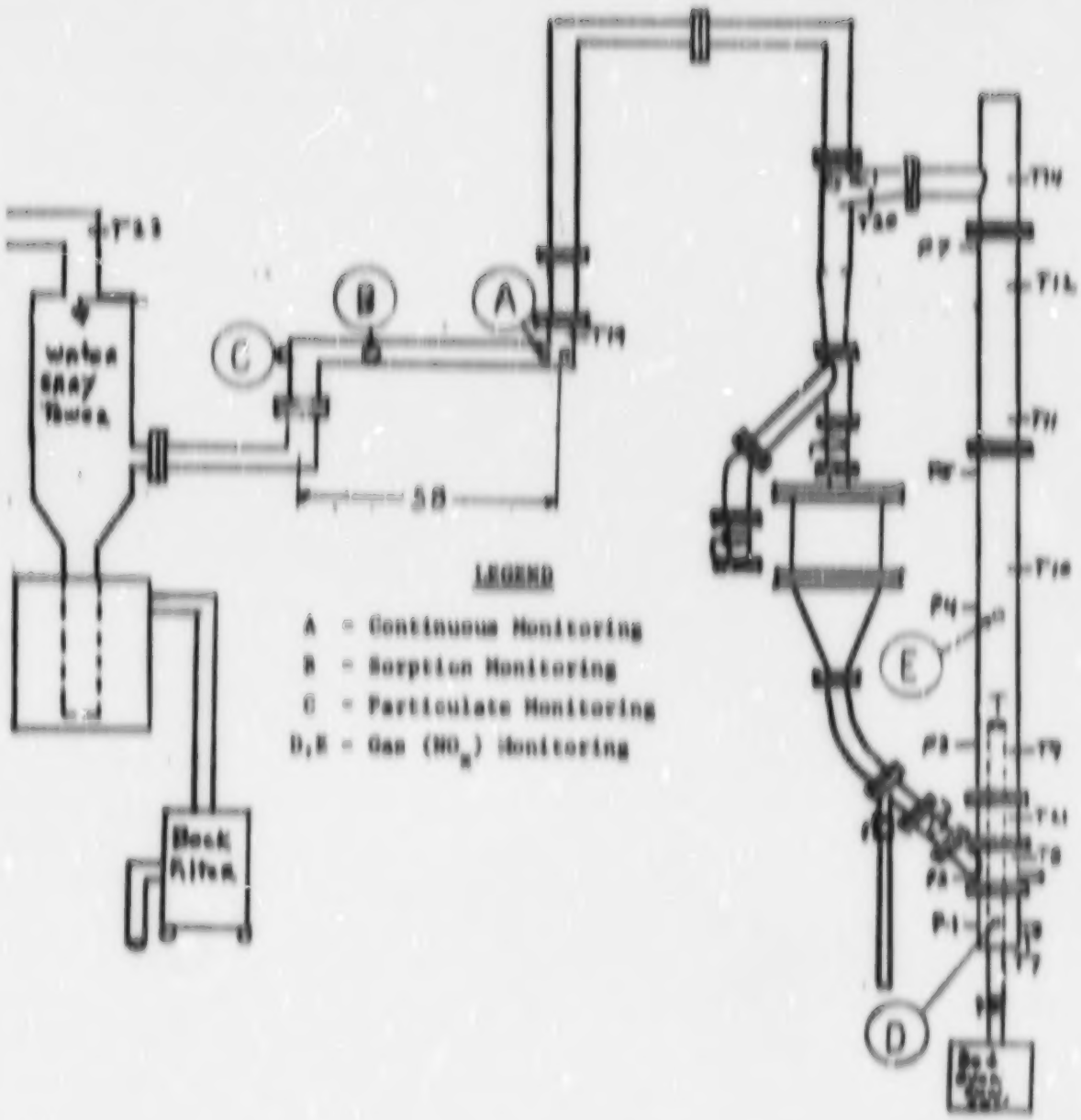

FIGURE 2. SCALE DRAWING OF 6-IN. FLUIDIZED-BED COMBUSTOR

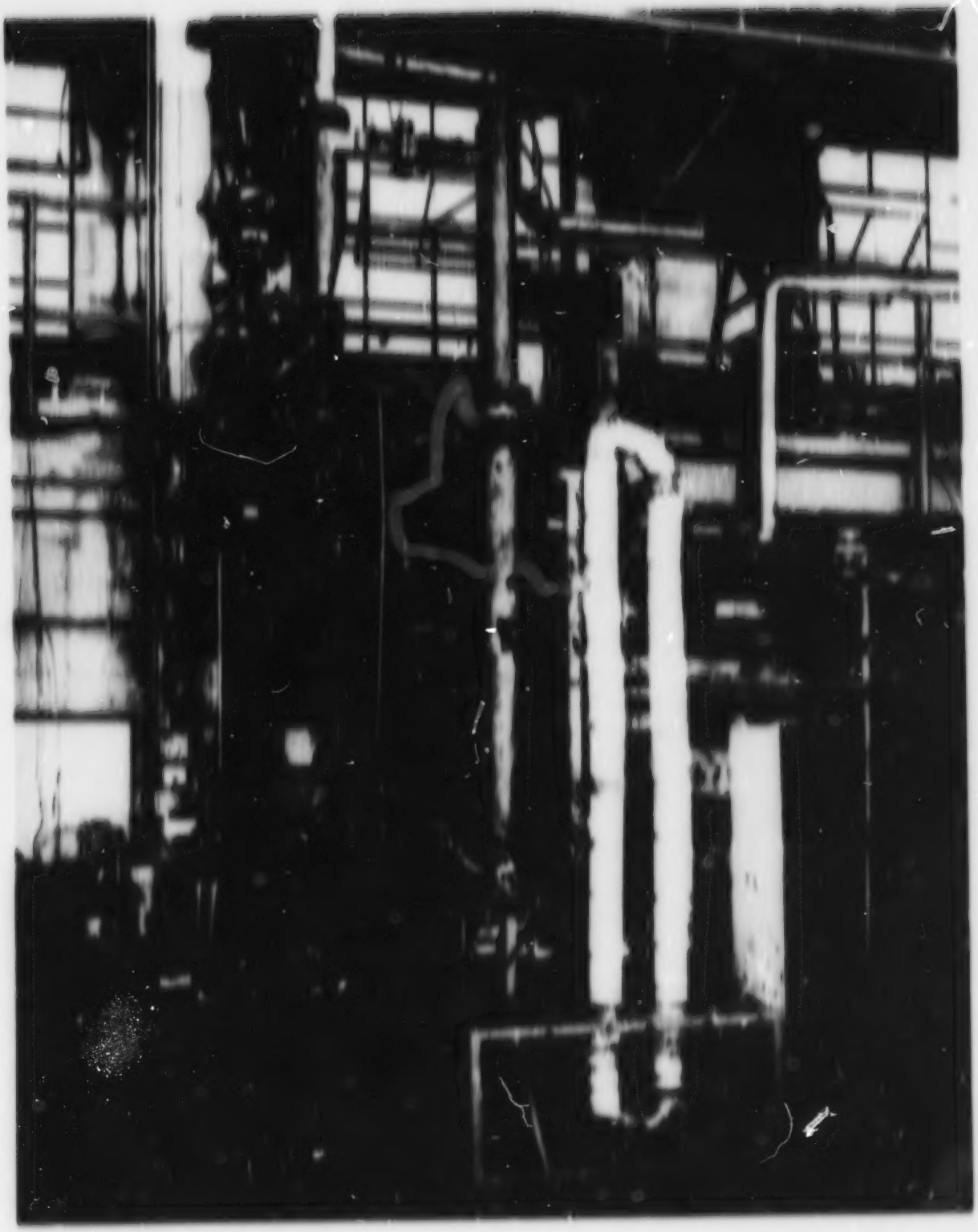

FIGURE 3. 6-IN. FLUIDIZED-BED COMBUSTOR

Sampling and Analysis Plan

The initial efforts in this program were directed to the development of a comprehensive sampling and analysis (S&A) plan applicable to fluidized-bed combustors and other coal burning units. The plan was developed around the design and operating features of the Battelle FBC unit. Since the Battelle unit is essentially a bench scale FBC model, many of the streams shown in Table 1 were not applicable to this unit. Notably absent from the Battelle unit were those streams relating to regenerative processes and fugitive emissions. Other streams were omitted on the basis of low priority. The streams chosen for sampling in this program were:

- Stack gas
- Particulate removal discard
- bed solids discard
- Prepared fuel feed to combustor
- Prepared sorbent feed to combustor
- Scrubber discard.

The S&A plan derived from the Battelle unit was refined and later finalized into the form shown in Table 3. The tabulation shows the streams sampled, the constituents measured in the streams, the analysis methods used, and the procedure used to obtain the sample. This plan was later generalized to include all streams likely to be encountered in FBC S&A programs. The generalized plan is given in the final sections of this report (Table 9).

Site Survey

A site survey is conducted prior to carrying out the S&A plan developed for the FBC unit. A site survey is an important part of the sampling program in that it provides proper coordination of the plant's physical layout with the test plan strategy. The more important points considered at the site survey inspection for this program were:

a. Are the sampling sites accessible and is there proper space allocation and supports (tables, platforms, etc.) for all the equipment and supplies?

b. Are there a sufficient number of sampling ports and do the sampling sites meet all the criteria for representative sampling?

c. Do the sampling sites have access to utility outlets of the number and type required by the sampling equipment?

TABLE 1. FBC SAMPLING — ANALYSIS PLAN

Level 1 — Scanning for Classes of Compounds

	Train and/or Sampling Method	Analysis Method	1976 Est. Cost
COAL			(320)
Proximate/Ultimate	Obtain three or four grab samples, ~100 grams each, at intervals during run and combine for representative bulk sample	ASTM D271	
Moisture			
Ash			
Volatile matter			
Fixed carbon (by difference)			
C, H, N, S, O (by difference)			
Sulfur – Total		ASTM D2492-68	
Pyritic			
Organic			
$SO_4^=$			
Trace metal		SSMS	
Na, Ca		AA	
Particle size		Sieve	
Heating value		Calorimeter/ASTM D2015-66	
LIMESTONE			(360)
Particle size	Obtain three or four grab samples, ~100 grams each, at intervals during run and combine for representative bulk sample	Sieve	
Ca, Mg, $SO_3^=$, NO_2^-, NO_3^-		AA – Spectrophotometric, phenol disulfonic acid	
Trace metals		SSMS	
OVERFLOW BED MATERIAL			(780)
Particle size (Chemical identification)	Collect all of overflow material; sieve for −325 mesh material; weigh −325 mesh sample and use for ash	Sieve	
Trace metals		SSMS	
$SO_4^=$, $SO_3^=$, F^-, NO_2^-, NO_3^-		Wet chemical methods	
Organic classes		Extraction/liquid chromatography/IR	
ASH			(780)
−325 mesh material from overflow bed material (weigh)		Sieve	
Trace metals		SSMS	
$SO_4^=$, $SO_3^=$, F^-, NO_2^-, NO_3^-		Wet chemical methods	
Organic classes		Extraction/liquid chromatography/IR	

	Tube and/or Sampling Method	Analysis Method	STD Sec. Sec.
[illegible]			[illegible]
C, H, N, S, O	1 gallon sample from scrubber at end of run; sample filtered and dried for 4 hrs at −100 F, remaining solid used for sludge sample; solution stored in capped bottle		
SO_2		Barium perchlorate titration	
NO_x		H_2O_2/Barium perchlorate titration	
Trace metals		[illegible]	
Organic Classes		Semivolatile Capillary chromatography/FID	
Gas or Vapor			[illegible]
1. Particulates (>0.3 μ)	Sections No. 1 repeated two or three times during run and at end of run; sample combined and stored in dark; alternate sequence for high-level materials; long-term sequence for low-level materials		
a. Trace metals		[illegible]	
1) All (Hg excepted)			
b. Minor elements (metals)		[illegible]	
1) Na, Al, Si, K			
c. Anions			
1) Chloride, Fluoride		[illegible]	
2) NH_3		[illegible]	
3) NO_2, NO_3		Spectrophotometric, phenol disulfonic acid	
4) SO_4^{2-}, PO_4^{3-}		Barium perchlorate titration (H_2O_2 with H_2O_2)	
d. Organics			
1-40 Organic classes		Semivolatile Capillary chromatography/FID	
41 TOC		Fluorescence – Section No. 2 above	
42 Organic-related other compounds (9 classes collected)		[illegible]	
e. C, H, N, S, O			
f. Size analysis		None	
2. Particulates (>0.3 μ, <2.5 μ)			[illegible]
a. Trace metals	Two M-5 trains, isokinetic sampling, approximately 2 hrs; sample taken from cyclones to M-5 trap and stored in dark	(as described in No. 1 above)	
b. Minor elements (metals)			
c. Anions			
d. Organics			
e. C, H, N, S, O			
f. Size analysis			
3a. Particulates <0.3 μ	Sample from [illegible] to M-5 trap, or separate impactor; sample stored in dark	(as described in No. 1 above)	[illegible]
a. Trace analyses as under Section 2)			

TABLE 3. (Continued)

	Train and/or Sampling Method	Analysis Method	1976 Sec. Cont.
3. Gases			(750)
a. Acid gases*			
1) CO_2	Continuous	NDIR	
2) SO_2	Continuous	NDIR	
3) $NO - NO_2$	Continuous	NDIR – Chemiluminescence	
4) SO_3		Colodyn-Ross	
b. Inorganic*			
1) CO	Continuous	NDIR	
2) O_2	Continuous	EC – Polarograph	
c. Organic			
1) Total gaseous hydrocarbon	Continuous or Bag	FID	
2) Organic classes: alkanes, alkylbenzenes, PAH, thiophenes, carbonates and esters, aldehydes, PCB, ketones, and alcohols	Sample stored in dark	Texas extraction/liquid chromatography/IR	
3) Organics – reduced sulfur (9 classes combined)	Bag or Texas	GC/FPD	
d. Hg, Cd, As, Pb, Se	10% HNO_3 or $K_2Cr_2O_7$ acid solutions; use H_2O_2 prior to solutions to remove SO_2; Solutions stored in dark	As	
e. HCl, HF, HCN, NH_3*	GaS absorption train (Figure 5 in text); 1.0% H, NaOH used to collect HCl and HF, 5% HOH solution for HCN and 10% H_2SO_4 to collect NH_3	Ion chromatograph (HCl, HF) and specific ion electrode (HCN, NH_3)	

* Level 2 scanning for specific compounds.

d. Do the sites meet critical OSHA requirements?

e. What arrangements must be made for transporting equipment from the ground to the sampling site?

f. Does the plant have adequate laboratory space available; if not, can the cleanup van be parked in close proximity to the sampling area?

g. Does the plant have personnel available to assist in the acquisition of solid and liquid samples?

h. What is the plants normal operating schedule and down-time of equipment?

i. What type and condition is the on-line measurement instrumentation?

j. Are support services available to the field team such as storeroom, welders, glass blowers, etc.?

Occasions may arise where other points may need consideration but these major areas should suffice for most FBC sampling programs.

Installation and Operation of Equipment

A wide variety of instruments and sampling units are required in sampling a FBC or other type combustion unit. Gas, liquid, and solid samples are generally involved. Some instrumentation is likely to be available and in operation at the plant site. If so, consideration should be made as to their suitability for use in the comprehensive analysis program.

Continuous Gas Monitoring--

Continuous gas monitoring instruments were available and in operation at the Battelle FBC unit and were used in this program for measuring CO, CO_2, SO_2, NO_x, O_2 and total hydrocarbons from the combustor. The instruments used for measuring each gas are given in the S&A plan shown in Table 3. Figure 4 is a schematic of the gas analysis system. The sample tubing to these instruments was made of stainless steel and/or Teflon and of proper diameter to allow sufficient gas flow to the instruments. Stainless steel tubing was installed at all sampling ports in preference to Teflon because of the somewhat high temperature for Teflon.

Calibration procedures were worked up for each instrument prior to the sampling runs. Flow rates to the instruments for either sample gases or span gases were adjusted to the needs of the instrument as specified by the manufacturer. Stainless steel bellows pumps were used to provide sample gases

to the instruments. Room temperature fluctuations were not a problem in our sampling, but temperature conditions must be considered if cold weather or wide fluctuations in temperatures are involved. Traps were used to remove particulates and moisture from the sample gas prior to entering the instruments. Pyrex wool served as a filter to remove the particulates and a wet- or dry-ice bath was used to effectively reduce the moisture content of the sample gas stream to an acceptable level for operating the instruments. (A word of caution here. While the removal of particulate and water vapor from the sample line is imperative to proper operation of most of the instruments, the total effect of the removal processes on the sampled constituents mainly, NO_2 and SO_2, is questionable. As noted later, more consideration should be given to the effects of the removal processes.)

Method 5 Sampler for Particulate and POM Samples--

Method 5 samplers, were installed to obtain particulate samples in this program. Modifications were made to the Method 5 sampler as follows, (1) installation of a small glass cyclone inside the heated chamber prior to the filter to further fractionate the particulates, and (2) installation of a tenax column downstream of the filter outside the heated chamber to collect POM samples.

A "Y" probe was constructed so that two Method 5 rigs could be used to sample particulates simultaneously from a single sampling point within the flue gas stream. Sample ports were installed so that samples could be taken at about midstream of the duct at least 10 tube diameters downstream from any elbows. Gas velocities were measured during the shake down run for isokinetic sampling. Operation of the Method 5 rig was in accordance with the Federal Register procedures (6), except no traverse of the duct was made.

Bubbler Samples--

In addition to the continuous monitors and the Method 5 rigs, sorption trains were constructed and used in this program for collecting acidic (HCl, HF, and HCN) and basic (NH_3) gaseous components present within the gas stream. Although not specifically required in a Level 1 analysis scheme, these sorption trains were installed to collect and analyze each of the gases for a more complete characterization of the emissions from the FBC unit. An oxidizing solution was also installed to collect certain trace metals that may be

present in vapor form in the stream. The metals of interest were Pb, Hg, Se, Te, Be, As, and Cd. Figure 5 shows a single typical absorption train used in the program.

Although SO_3 can also be collected in solutions such as alcohol-water mixtures, it was decided that the Gökscyr-Ross method would be the better one to use for SO_3 since much of the alcohol-water solution would evaporate over a two-hour period. Therefore, the Gökscyr-Ross apparatus was installed in place of a sorption train to collect SO_3. The manifold and sample line to the Gökscyr-Ross unit beyond the manifold were heated with heating tape, to prevent H_2SO_4 condensation. It is important that these areas be heated to at least 325 F to avoid loss of SO_3 (as H_2SO_4).

Shake Down Runs

Unless the FBC unit has been run previously at the desired operating conditions, it is generally worthwhile to make at least one preliminary or shake down run prior to the actual sampling runs. In so doing, the technicians operating the fluidized-bed unit are able to check their calculated values for producing the desired bed temperature and gas flow rates, SO_2 levels, excess air, etc., and make appropriate adjustments where needed prior to the actual sampling run.

Shake down runs were made prior to the sample Runs 1 and 2 in this program. Fluidized-bed operation was checked out and proper adjustments made. The technicians taking the samples were then able to make preliminary checks on the sampling conditions of the unit under the desired operating conditions. Appropriate temperatures of the various sampling ports were checked and gas velocities measured, where necessary, to allow for isokinetic sampling during the actual sampling runs. Instruments were checked out for proper operation and checks were made for leaks in the sampling units. At the completion of each shake down run, the FBC unit was prepared for the sampling run which followed the next day.

COLLECTION AND PREPARATION OF SAMPLES FOR ANALYSIS

Details of the procedures involved in obtaining, handling, and preparing samples for analysis from our fluidized-bed combustor are discussed in reference to the sampling and analysis plan shown in Table 5. This plan was closely followed in each of the sampling runs made.

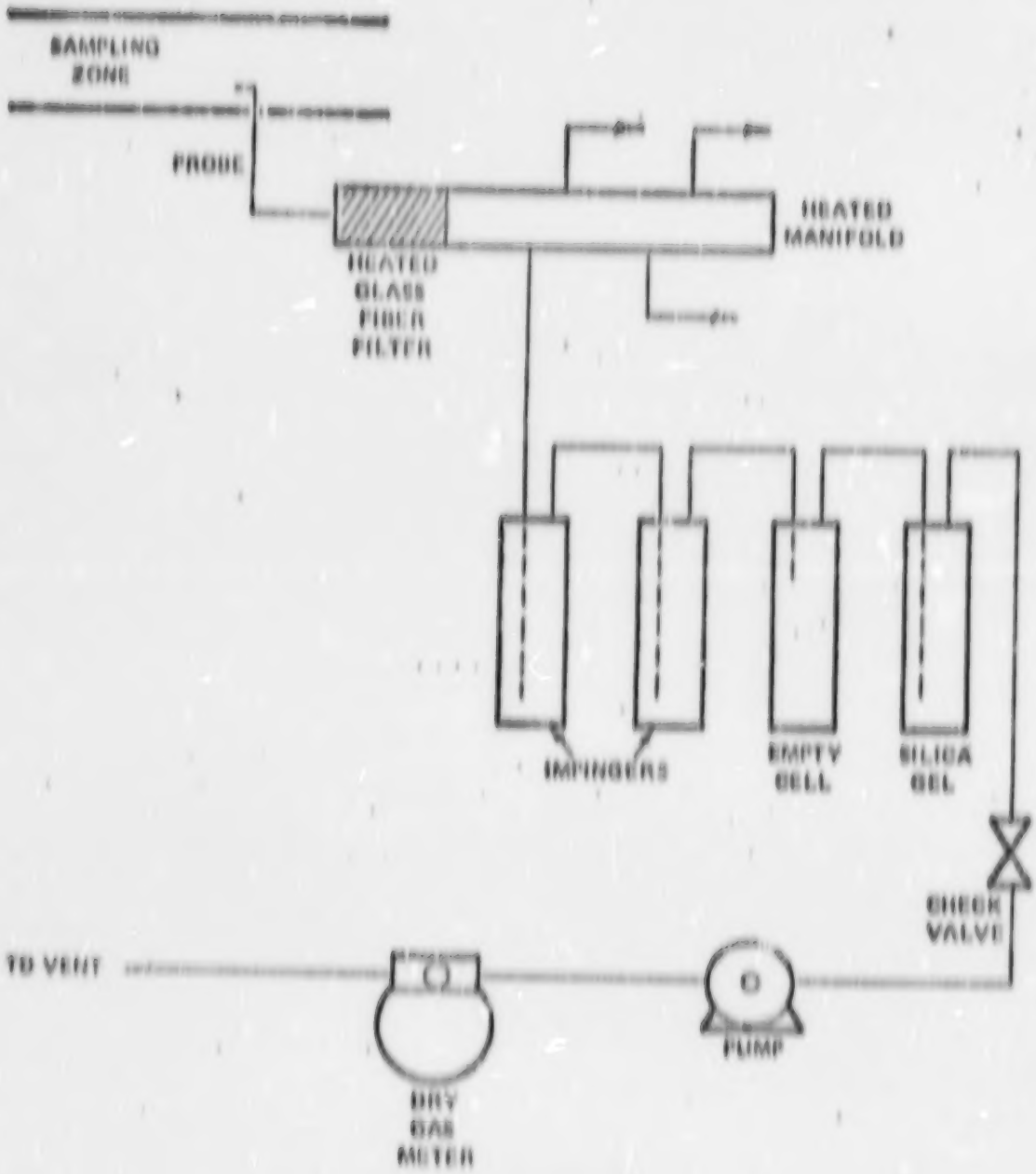

FIGURE 5. TYPICAL GAS ABSORPTION TRAIN

Sampling

Samples were taken from the various selected streams after stabilizing the FBC unit at the desired firing conditions. Sampling was started after the SO_2 level in the gas stream was reduced to the desired level, approximately 700 ppm, via reaction with the limestone. Six major streams were sampled as indicated earlier. The sampled streams are discussed in the order given in Table 3. Figure 6 is a schematic outline of the sampling locations in the FBC unit. Each sample stream discussed below is numbered in accordance with the numbered locations in Figure 6.

(1)-Coal Feed Stream--

Three or four grab samples of coal, about 100 grams each, were taken at about equal time intervals over the 2-hour sampling period. The crushed coal was fed to the FBC unit on a small conveyor belt. Since the unit burned only about 15 lb/hr or less of coal, the coal stream to the unit was small and cross-section samples of the stream were used as representative of the coal mass. In larger units where much more coal is used, the procedure for collecting a representative coal sample is more involved. The proper procedures have been noted in an earlier section of this report.

The 3 or 4 grab samples of coal were combined, as the run progressed, in a single plastic container and, at the end of the run, the total sample was sealed in the plastic container and stored.

(2)-Limestone Feed Stream--

The limestone was also fed to the FBC unit on a small conveyor belt and samples of limestone were taken in the same manner as for coal. The total sample was sealed in a plastic container and stored. As with the coal, the large combustors would require more detailed sampling procedures.

(3)-Overflow Bed Material--

This material consisted mostly of limestone and was continuously sampled through the overflow pipe in the reactor bed during the entire 2-hour sampling period. A representative sample was taken from the overflow container at the end of the run. This was done by scooping samples from various part of the mass bed material and combining them in a plastic container. The container was sealed and stored in the dark. (All samples to be analysed for POM and other organics were stored in the dark to minimize decomposition.)

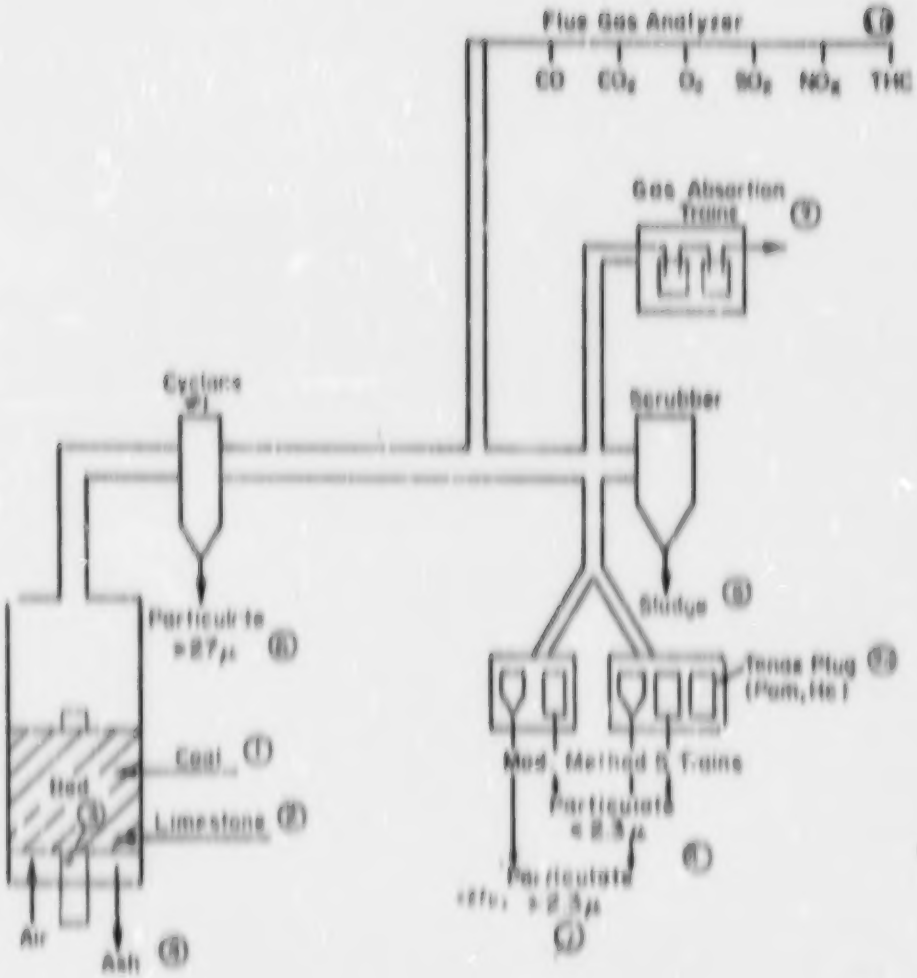

FIGURE 6. SCHEMATIC OUTLINE OF FLUIDIZED-BED COMBUSTION AND SAMPLING LOCATIONS

(4)-Ash--

The ash sample referred to here was taken from the overflow bed material. It is the small -325 mesh particles remaining in the overflow bed material at the completion of the run. All of the overflow bed material was sieved at the end of the run into several size fractions. The smallest fraction (-325 mesh) was used as a representative ash sample from the bed material. Generally less than 0.1 percent of the total overflow bed material remained in this smallest fraction. However, sufficient sample was obtained in most runs for the proper analysis. The ash sample was sealed in a plastic container and stored in the dark.

(5)-Sludge--

The sludge sample is the solid material caught in the water scrubber attached to the end of the flue gas stack. In obtaining a sludge sample, the water used for scrubbing the flue gas was continuously removed from the scrubber barrel and passed into a large centrifuge. The centrifuge was lined with a fine filter which retained the solid material while passing the liquid. The centrifuge was run during the entire sampling period. Several liquid filtrate samples (about 1 gallon each) were taken from the centrifuge drain at recorded time interval during the run and stored in large plastic bottles. The solid material remaining on the filter was removed by scraping; the solid sample was dried and sealed in a plastic container and stored with the other samples in the dark.

(6) through (9)-Flue Gas Stream--

A large number of samples was taken from the flue gas stream. Samples were obtained from the in-stream cyclone and from two Method 5 rigs, several sorption trains and a number of continuous monitors. Particulate and gaseous samples were involved. Sampling procedures are described below.

(6), (7), and (8)-Particulate--Particulate samples were obtained from two sources (1) the solid material removed by the cyclone in the flue gas stream, and (2) from samples taken by the Method 5 rigs. The cyclone and Method 5 rigs provided three size fractions of particles. These were (approximately as calculated from cyclone dimensions),

1. Particles greater than 37 μ diameter

2. Particles less than 27 μ greater than 2.3 μ diameter

3. Particles less than 2.3 μ diameter (0.1 μ limit).

The larger cyclone, which was a part of the flue gas stream, removed the larger particles (>27 μ). A smaller cyclone installed in each Method 5 rig removed the intermediate size particles (<27 μ , >2.3 μ). The filter in the Method 5 rig removed the remaining particles down to about 0.1 μ.

Samples from the larger in-line cyclone (>27 μ) were withdrawn from a particulate collection chamber at the bottom of the cyclone at the end of the 2-hour run. The samples were sealed in a plastic bottle and stored in the dark.

Particulate samples <27 μ, >2.3 μ were obtained from the cyclone in the Method 5 rig under the following conditions.

1. Method 5 (isokinetic) sampling procedure was used.
2. Sample was collected at midstream of 4-in. diameter stainless steel duct at a position about 1-ft from end of duct (sample point C in Figure 2).
3. Heated stainless steel tubing, 1/2-in. I.D. was used to withdraw sample from stream into Method 5 rig at the rate of about 0.75 cfm (using appropriate size nozzle to obtained desired isokinetic flow rate).
4. Particulate samples were collected for period of 2 hours.
5. Samples were taken from cyclone in Method 5 rigs after run was completed.
6. Samples were stored in sealed glass containers in a desiccator (in the dark and under N_2 gas if stored for several days). Particulate samples were combined for analysis if more than one sample taken during run.

A problem was encountered in the separation of particle sizes. The designated fractions were not always obtained from the Method 5 rig samples since the smaller cyclone tended to clog rendering the separation meaningless. In those instances, the filter and cyclone samples from the Method 5 rig were combined to form a less than 27 μ fraction. Particulates were also washed from the sample probe with acetone followed by wash with methylene chloride. These samples were dried and added to the <27 μ catch. Filter samples in the Method 5 rig were removed when filter loading became sufficiently high. The filter and loading were weighed and placed in a glass container, sealed and desiccated. The samples were removed from the filter prior to analysis by flexing

the filter material; this released most of the caked-on sample. The filters were reweighed and particulate sample weight determined. All particulate samples were stored in glass containers, and placed in desiccators in the dark.

(9)-Impinger Samples--These samples were obtained by sorption of a particular constituent in a solution which efficiently trapped the desired material. For each sorption train, two solutions were used in series to insure more complete removal of the desired constituent. The second solution collected only a small fraction of the total sample (<10 percent). The impingers were immersed in wet ice for better sorption of samples. Each unit (sorption train) was operated independent of each other. Flow rates and total gas sampled were recorded in each sorption unit. Pumps were downstream of the bubblers and all gases were dried with drierite prior to entering the pumps. Sampling rates were about 0.2 cfm; the sampling period was usually 2 hours. Approximately 10 to 30 cubic feet of gas passed through each bubbler.

At the end of a 2-hr sampling period, the solutions were removed from each impinger and placed in a separate glass bottle. Volumes were measured and samples were stored in a cabinet at room temperature until ready for distribution and analysis.

The Greenburg-Smith unit was washed with distilled water then 3 percent peroxide solution and acetone to remove the SO_3 (as H_2SO_4). The volume of solution was recorded and the sample stored with the above impinger samples.

(9a)-POM--POM samples were collected on a tenax column attached to the sampling line of the Method 5 rig downstream of the filter. The tenax column was covered at all times to keep out light. At the end of the run, the column was removed and filled with nitrogen, sealed and stored in a refrigerator (kept in the dark at all times).

(10)-Gases--

The remaining samples from the flue gas stream involved essentially the gaseous species in the stream. The acid gases CO_2, SO_2, and NO_x-NO_2 and the inorganic gases CO and O_2 were monitored continuously as described earlier. Total hydrocarbon content was also monitored continuously.

Sampling Problems

A few problems were encountered in the sampling of the Battelle FBC unit. These, however, were generally isolated events and produced no threat to the completion of the sampling task. The specific problems encountered were:

- Small cyclones in Method 5 rigs tended to clog after several minutes of sampling rendering particle size separation incomplete.
- Flue gas temperature at sampling port dropped below that desired for good SO_3 sampling (325° F) for Runs 2 and 3.
- Filters would load heavily by end of a 2-hour run. Some had to be replaced during the run (Method 5 rig).

Labeling

Proper labeling of samples is a very important part of the sampling program. Each sample in each stream listed in Table 3 was labeled so as to identify the stream sampled, material or sample collected, run number and date of run. With proper sample labeling, no confusion will result in relating the analytical results to the appropriate sample. It is equally important that starting and finishing times for all processes be noted and coordinated with the individual collection processes for each sample category so as to provide valid comparison of all pertinent data.

Analyses of Samples

Analyses charts were drawn up for each run relating the sample taken from the FBC unit to the analyses to be made on the sample. An example chart is shown in Table 4 for Run No. 2 samples.

As shown in Table 4 each original sample was divided into a number of smaller fractions so that sufficient material was available for the different analyses needed on each sample. The number of fractions of each sample needed is indicated by the number of "forks" or divisions after each original sample (shown in boxes) in Table 4. Each fraction of sample was weighed to the nearest 0.1 gram before distribution for analysis. In the case of solutions, the volume of each solution was recorded prior to distribution for analysis.

Additional Considerations in the Analyses of Samples

Three other analysis areas not shown in the analyses chart of Table 4 but which should be considered in a FBC sampling program are (1) biological testing, (2) radioactivity measurements, and (3) noise measurements. Areas

TABLE 4. SAMPLE IDENTIFICATION AND ANALYSES

Material	Fluid-Bed Sample No.	Sample Number Designation	Analyses
Illinois #6 coal (-8 M)	[illegible]	[illegible]	Proximate/ultimate: (1) Moisture (2) Ash (3) [illegible] (4) Diff. difference; (5) Volatile matter (6) Fixed carbon (by difference); (7) Total (8) Pyrites (9) Organic (10) $SO_4^=$
			Sulfur
			Na, Ca
			Heating value
			Trace metals
			Particle size
Grove limestone	[illegible]	[illegible]	Ca, Mg, $CO_3^=$, NO_2^-, NO_3^-
			Trace metals
			Particle size
Bed material	[illegible]	[illegible]	Trace metals
			Organic classes
			$SO_4^=$, $SO_3^=$, $S^=$, NO_2^-, NO_3^-
			Particle size
Ash (-325 M)	[illegible]	[illegible]	NO_2^-, NO_3^-, $S^=$, $SO_4^=$, and $SO_3^=$
			Fusion temperature
			Trace metals
			Organic classes
Sludge	[illegible]	[illegible]	C, H, N, S, O, $SO_4^=$, and $SO_3^=$
			Trace metals
			Organic classes
Flue gas stream Particulate [illegible]	[illegible]	[illegible]	Trace metals (approx 60 metals)
			C, H, N, S, O
			Anions: NO_2^-, NO_3^-, $SO_4^=$, $SO_3^=$
			Organic classes
			FOM
		Particulate size	Organic and reduced sulfur compounds

TABLE A.

Material	Fluid-Bed Sample No.	Sample Number Designation	Analyses
Flue gas stream Particulate [illegible] (If two particulate fractions involved here, [illegible] and [illegible] smaller fraction is designated batch No. [illegible] and same analyses as [illegible])	[illegible]	[illegible]	Trace metals
		[illegible]	[illegible]
		[illegible]	Anions, [illegible]
		[illegible]	Organic classes
		[illegible]	PDM
		Particle size	Organic and reduced sulfur compounds
Flue gas stream Gases	[illegible]	[illegible]	Organic classes
			PDM
			Organics - reduced sulfur
		[illegible]	HCl, HF
		[illegible]	HCN
		[illegible]	NH_3
		[illegible]	Trace elements (solution)
		[illegible]	SO_3 (Onkeyr-Ruse)
Gases, continuous monitoring	[illegible]	[illegible]	O_2
		[illegible]	CO_2
		[illegible]	CO
		[illegible]	SO_2
		[illegible]	NO_x
		[illegible]	NO

1 and 2 are included in the general sampling and analysis plan in Table 9 in a later section of this report. Although samples were available for analysis from our sampling program in areas 1 and 2 above, no testing or measurements were made in our laboratories. However, samples were sent to EPA for biological testing. On the other hand, noise measurements were made in the area of the 6-in. FBC unit used in this program. The results are included in the appendix. Further discussion of noise analyses and areas 1 and 2 above are given in the "Recommended Sampling and Analysis Plan" section.

Analyses Problems

No serious problems were encountered in the analysis of samples taken in this program. The determination of the concentration of a species "by difference" (e.g., the oxygen values in some of the samples in Table 4) is likely to produce more error than the direct measurements made on other species. But this would be expected from the procedure involved.

SECTION 4

EVALUATION OF EMISSION DATA

Three runs were made in the course of this sampling program. These are designated Run Nos. 1, 2, and 3. The firing conditions for each of these runs differed as indicated in the following tabulation.

	Run No. 1	Run No. 2	Run No. 3
Coal feed rate, lb/hr	15.9	8.8	9.3
Limestone feed rate, lb/hr	15.4	4.3	8.1
Air feed rate, lb/hr	145.0	87.3	84.2
Bed height: expanded, inches	48	48	48
settled, inches	12.6	21.6	21.6
Bed temperature, F	1538	1655	1490
Superficial gas velocity, ft/sec	9.1	6.0	5.3
Ca/S ratio	6.7:1	2.9:1	7.1:1
Particulate loading, g/m^3	1.44	1.64	NA

Sampling procedures were the same for Run Nos. 2 and 3, but different slightly between Run Nos. 1 and 2, as did also some of the analyses procedures between these latter two runs. These differences are brought out in the list shown in Table 5. The changes were made to bring about a more cost effective sampling and analysis plan while at the same time completely defining the major pollutants emitted from the FBC unit.

Two of the three runs, Runs 1 and 2, were selected for analyses. The results of the analyses of these samples are presented in the Appendix, along with the firing conditions for each of the Runs 1, 2, and 3.

The primary purpose of the Runs 1 and 2 data presented in the Appendix was to reduce the practice the various sampling and analysis procedures under actual fluidized-bed operation. Although FBC emission data are

TABLE 5. CHANGES MADE BETWEEN RUN NOS. 1 AND 2

Change Made	Reason for Change
1. Proximate/ultimate analysis made on bed material -325 M in Run No. 1; discontinued in Run No. 2	Analysis of little use
2. Na, Al, Si, K, Cl^-, F^- analyzed individually (e.g., atomic absorption, ion electrode, etc.) in bed material samples in Run No. 1; determined these elements by XRFS in Run No. 2	More efficient, eliminate duplication
3. NO_3^-, $SO_4^=$, $S^=$, and $CO_3^=$ anions added to the analysis of bed material and particulate samples in Run No. 2	More completely define anion concentrations in solid samples
4. Analysis for PCM increased to include bed material, sludge, and particulate samples in Run No. 2	More completely define the PCM levels in solid samples
5. Organic class analyses increased to include bed material and sludge samples in Run No. 2	More completely define organic classes in solid samples
6. Increased analysis of trace elements to include sludge samples in Run No. 2	To better define trace elements in effluent waste material
7. Increased particle size analysis to include bed material and particulate (both >37 and <37 microns) samples in Run No. 2	To define particle size ranges more completely
8. Reduced quantity of solid sample for bioassay from 20 grams in Run No. 1 to 2 grams in Run No. 2	Only 2 grams of sample needed for analysis

currently quite limited, the data obtained in Runs 1 and 2 also merit some evaluation in terms of other coal burning emissions -- both fluidized-bed and pulverized coal combustion emissions. Tables 6, 7, and 8 present such comparisons.

General

In Table 6 some average comparisons are made between the Run 2 FBC emission data and some small scale pulverized coal (PC) firings (8). The latter were data obtained by Battelle on another EPA program, Contract No. 68-02-2119, concerned with the combustion of specially treated coals. The pulverized coal (PC) data shown are for raw (untreated) coals with sulfur contents of about 2 percent. (We have directed our attention to Run 2, rather than Run 1 here, because it was at a higher temperature, about 1655 F.)

As regards the gaseous emissions, the principal differences are in the CO and SO_2 emission levels. SO_2 levels are noticeably lower in the FBC operation, as expected, due to the capture of SO_2 by the limestone. The limestone capture efficiency in Run 2 for a 4.1 percent sulfur coal was about 67 percent.

The high CO levels in FBC operation compared with pulverized coal firing is another characteristic, so to speak, of FBC. The high CO levels in the FBC run here also go hand-in-hand with high hydrocarbon emissions and possibly with low NO_x emissions. Hydrocarbon emission in PC firing are usually quite low and therefore are often not even measured.

It is sometimes stated that NO emissions from FBC operations are lower than from PC firings. The data in Table 5 neither support nor contradict that statement. In a recent study on FBC NO_x emissions under Contract No. 68-02-2138 we also point out this disparity (9).

Particulate loadings (particles <27 microns, particles that pass the first cyclone) appear quite similar for FBC and PC firings. The same can be said for POM loadings and for the ash analyses - within the limits that one can compare data from a single FBC run.

Trace Elements

Table 7 shows a comparison of trace element data from an Illinois No. 6 coal (the same type coal as used in this study) and its ash. The analyses

TABLE 6. COMPARISON OF DATA FROM FLUIDIZED-BED AND PULVERIZED COAL COMBUSTORS

	FBC Run 7	PC
Gases		
O_2, %	3.6	2-10%
CO_2, %	17.3	13-15%
CO, ppm	2090	90-300
SO_2, ppm	730	1200-1500
NO_x, ppm	350	200-700
HC, ppm(C)	360	NA
Particulate		
Loading, mg/m^3	1640 (1500)*	1000-6000
PAH, ug/m^3	5 (72)*	0.1-65
Ash		
C, weight percent	8-20%	high, to 90%
H	.25%	0.3%
N	0.1-0.3%	0.1-0.4%
S	4-6%	1-3%

* Run 1.

TABLE 7. COMPARISON OF TRACE ELEMENT DATA FROM COAL AND ASH OF ILLINOIS NO. 6 COAL

Element	PPM					
	COAL			ASH		
	ANL	BCL		ANL	BCL	
		Run No. 1	Run No. 2		Run No. 1	Run No. 2
As	2.1	2.7	<3			
Be	1.6	0.17	2	13	2.6	0.20
Br	4.1	4.7	10			
Ce				38	15	50
Co	3.2	4.0	10	34	2.1	10
Cr	22	13	100	800	15	100
Dy				8.5	1.4	3
Eu	0.2		<0.5			
F	79	110	83	5.2	290	85
Fe($\times 10^4$)(a)	1.2	>1	~5	13	>1	~2
Hg	1.2	0.16	<2	0.007	<0.01	<0.3
K($\times 10^3$)(a)	1.5	1.2	~6	16	>5	~10
La	3.9	5.0	20	40	6.4	50
Mn	19	80	100	160	60	200
Na($\times 10^2$)(a)	3.0	8.9	200	27	~14	30
Pb	8.0	0.47	<1	46	4.3	20
Sc	3.1	1.6	3	34	1.6	30
Sm	0.005	0.71	<1			
Tb				3.1	0.19	0.5
Yb	1.4	0.23	0.5	11	1.6	1

(a) Indicates values in table that are to be multipited by the factor shown, e.g., 1.2 is 12000 ppm Fe.

TABLE 8. COMPARISON OF TRACE ELEMENTS IN COALS AND COAL PRODUCTS (μg/g)

Element	Coal: ANL Run TR 3 (a)	Coal: BCL (b) Run No. 1	Coal: BCL (b) Run No. 2	Coal: Power Plant	Coal: Mean Value (c)	Final Ash: ANL Run TR 3	Final Ash: BCL Run No. 1	Final Ash: BCL Run No. 2	Power Plant Sample 8A
As	5	2.7	<3		14	3.5	0.07	1.0	15
Ba		35	300				180	300	
B		95	<0.03				31	5	
Be	0.7	0.17	3		1.6	0.8	<0.18	<0.005	
Br	13	4.7	10		13		4.5	1.0	
Ce		9.8	50				13	3.0	
Cd		0.10	<30				0.14	<10	
Co	1.8	4.0	10		0.6		0.14	0.3	
Cr	100	13	100		14	13	1.3	10	
Cu		9.0	30	9.6			78	3	83
Dy	0.3	0.70	<1				0.49	<0.3	
Eu			<0.5				0.25	<0.3	
F	25	110	<3		61		170	<3	
Fe(x10⁴)(d)	1	>1	>5	0.37	1.9	35	0.68	>0.10	8.6
Hf		0.18	<2			96	1.1	<0.5	
Hg	0.15	0.16	<3	0.070	0.3	<0.005	<0.01	<0.3	0.160
K(x10³)	3.8	1.2	>6		1.6	0.66	>1.6	>2.0	
La	4.5	3.0	30			3.7	0.4	3	
Li		0.13	30				3.7	1	
Mn	36	80	100		49	39	26	30	
Mo		3.9	30	0.99			1.3	<3	3.9
Na(x10³)	6.9	8.9	200		3	13	3.2	3	
Ni		33	<10				3.3	<3	
Pb	35	0.67	<1		35	31	1.9	1	
Sb	0.3	0.56	<0.5		1.3	0.7		<0.3	
Sc	1.7	1.6	3			1.8	0.16	1.0	
Se		0.39	<5	1.9				<3	7.7
Sm	0.8	0.71	<1			0.1	0.03	<0.5	
Th			<0.3					<0.1	
V		30	500				7.0	10	
Yb	<1	0.33	<0.5			0.3	<0.49	<0.3	
Zn		37	<10	7.5			17	<3	30
Zr		10	300	13		300	36	30	330

	Primary Cyclone				Secondary Cyclone			
	AML Run TR 3	BCL Run No. 1	BCL Run No. 2	Power Plant Sample 1A	AML Run TR 3	BCL Run No. 1	BCL Run No. 2	Power Plant Sample 2A
Element								
As	25	4.1	1.0	44		6.1	3	180
Ba	450	180	500		960	320	500	
B		500	50			2000	300	
Be	0.6	2.6	0.20		6.0	6.0	2	
Br		6.0	0.50		3	60	1	
Ca	19	15	50		13	44	50	
Cd		0.67	<3			1.0	<3	
Ce	11	2.1	10		19	24	10	
Cr	180	15	100		200	87	190	
Cu		69	50	150		190	50	210
Dy	1.8	1.4	3		2.9	2.0	3	
Eu		0.50	1			0.94	1	
F	30	200	<5		10	450	<20	
Fe($\times 10^4$)[d]	3.9	<1	<2	7.0	3.6	<1	<2	6.9
Hf	2.9	1.8	2		6	1.8	<0.5	
Hg	0.46	<0.01	<0.1	0.026	0.46	.14	<0.1	0.510
I($\times 10^3$)	3.7	<5	<10		3	<10	<20	
La	31	6.4	50		53	30	50	
Li			10			37	20	
Mn	110	60	200		140	60	500	
Mo		3.3	20	11		14	10	41
Na($\times 10^3$)	41	<14	30		73	<50	37	
Ni		23	200			99	100	
Pb	95	4.3	20		260	43	100	
Sb	3	0.67	0.2		6.3	1.4	1	
Sc	9	1.6	30		19	7.3	50	
Se		0.94	<5	4.1		9.4	<5	27
Sm		1.7	5			3.6	3	
Th		0.19	0.5			0.46	0.3	
V		23	500			140	1000	
Yb	4	1.6	1		7.5	3.5	1	
Zn		67	<3	100		140	<3	390
Zr		35	300	260		120	300	310

(a) Run TR 3 bed temperature 1900 F; Asburight coal used.
(b) Run No. 1 bed temperature 1900 F; Run No. 2 bed temperature 1655 F; Illinois No. 6 coal used.
(c) Mean analytical values for constituents in 101 different coals.
(d) Recorded values to be multiplied by 10^4, e.g., reported value of 1 is really 10,000 ppm.

were determined by Argonne National Laboratory (ANL) (10) and BCL. The ash from the burned coals were obtained from different combustion processes. The ash material analyzed by ANL was from an unquenched gasifier ash of the coal while ash analyzed by BCL was from the primary cyclone of the FBC unit. The BCL analyses were spark source mass spectrometric analyses; the ANL group used different analytical techniques in their analyses; these include wet chemical, atomic absorption, fluorimetry, specific ion electrode, and neutron activation analysis.

Approximately 2/3 of the BCL and ANL trace element coal analyses agree within a factor of three. Those elements showing deviation greater than a factor of three include Be, Hg, Mn, Pb, Sm, Yb, Cr, F, La, and Na. Manganese and lead are the only elements showing large deviations common to BCL Runs 1 and 2. The mercury values in the ANL data are reported as not representative of the coal seam.

Considering the possible difference in coal samples, the non-statistical approach to these analyses, and the different analytical techniques used, the agreement of data in the majority of the elements is satisfactory.

Most of the elements reported in the ash of BCL Run No. 1 and the ANL run deviate by more than a factor of three. The elements showing large deviations are Be, Co, Cr, Dy, F, Fe, La, Pb, Th, and Yb. On the other hand, all but five of the elements reported in BCL Run No. 2 ash data agree within a factor of three with the ANL data. Those elements showing greater than factor of three deviation are Be, Cr, Fe, Th, and Yb, all of which are also common to the elements showing large deviations in Run No. 1

One would not necessarily expect the data from the various ash samples to agree as closely as in the case of coal, since the ash samples were taken from two different combustion processes (as mentioned above) and probably are not comparable in particle size. The BCL ash sample contained particles greater than 37 microns. The ash size is not reported for the ANL data. Considering the possible difference in ash sample and the different analytical techniques, the ANL and Run No. 2 data are in fairly good agreement.

Table 8 offers an interesting comparison of trace element data from fluidized-bed and pulverized coal combustors. These data are derived from the ANL pressurized FBC study (10), a coal-fired power plant study (11) and the present FBC study. The ANL study was carried out in a 6-inch diameter pressurized fluidized-bed combustor, quite comparable to Battelle's unit except the ANL unit was operated at about 8 atm absolute pressure. The coal-fired power plant data were obtained from samples from the 180 MW Unit No. 3 of Public Service Company of Colorado's Valmont Power Station near Boulder, Colorado.

In the Table 8 data, different coals were used by ANL and BCL in firing the fluidized-bed combustors. ANL used an Arkwright coal and BCL an Illinois No. 6 coal. However, the bed temperatures for ANL Run TR3 and BCL Run No. 1 were the same, 1360 F. Data from combustors other than FBC units are also included in Table 8.

In summary, the comparison of the emission data in these studies bears out the reduction to practice of the comprehensive sampling and analytical techniques developed here for fluidized-bed combustors. The data presented here however should only be used at this time for the purpose of evaluating the sampling and analysis technique. This program was not designed for statistical evaluation of the data. The data presented in the two reference studies selected here for comparison should also only be accepted at face value.

SECTION 5

RECOMMENDED SAMPLING AND ANALYSIS PLAN

The generalized S&A plan for fluidized-bed units is presented in Table 9. This plan is similar to the one presented in Table 3 with appropriate additions in Table 9 to include those sample streams not covered in sampling the Battelle FBC unit. Table 9 lists all the main streams to be considered in sampling a FBC unit, specific pollutants involved, collection technique, analysis method and level approach.

Two areas of analysis shown in Table 9 which may require further brief comment are the biological testing and radionuclide measurements. In reference to biological testing, currently it is felt that five tests of a screening nature are available to evaluate cytotoxicity, mutagenicity, and carcinogenicity. These tests are:

1. Ames' bacterial mutagenesis toxicity assays
2. BCL - prescreen toxicity assay (Hamsaiton cells - BALB/c 3T3)
3. BALB/c 3T3 clonal transformation assay (mouse fibroblast cell)
4. C3H 10T 1/2 mouse prostrate cell assay
5. Syrian hamster embryo clonal transformation assay.

A more detailed description of the assay options available is presented in the Battelle report referenced earlier.

Radioactive content of samples should be considered in an overall sampling program. It is suggested that a low background proportional counter be used to make the measurements. The proportional counter gives a measure of the gross α and β emissions from thorium, uranium, radium, and their decay products in the samples being analysed. The instrument is highly sensitive and can detect radioactivity levels below a picocurie (10^{-12} curies).

Some of the procedures involved in the analysis of other components shown in Table 9 have been discussed previously. Other analytical procedures

TABLE 9. SAMPLING AND ANALYSIS MATRIX FOR COMPREHENSIVE ANALYSIS OF FSC STREAMS

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can be obtained from the reference methods given in the table; some are simply standard calorimeteric or titration procedures for the listed component.

One other area to be considered in the environmental assessment of a FBC unit is the noise generated by the unit and its associated components. The analysis should include an inventory of all significant noise sources. Noise emission data would be obtained for each source through direct measurement and/or from available literature. An integrated noise effect, taking into account transmission paths and isolation, would be generated from appropriate existing computer programs. One can develop a map of noise intensity within and exterior to the plant.

Table 9 is suggested for use in planning an effective sampling and analysis program for specific fluidized-bed units. Proper selection of streams and pollutants to be measured can be obtained from Table 9 (with the necessary prior information on the FBC unit). One can then proceed to sample the FBC unit and develop an analysis scheme, such as shown in Table 4, for each stream sampled.

AREAS NEEDING FURTHER STUDY AND/OR CONSIDERATION

In the course of this program, it became apparent that certain areas involving (1) the sampling and analysis of samples, (2) the associated costs and timing involved in carrying out a sampling program, and (3) the Level 1, 2, 3 approach to sampling should receive further consideration. Specific areas of concern are presented below:

1. Two questionable areas were encountered in SO_3 sampling -- (1) the accuracy of the Gökseyr-Ross method in determining SO_3 levels, and (2) the importance of flue-gas temperature in sampling SO_3. The wide variation in SO_3 levels encountered in this sampling program suggests that both the collection method and flue-gas temperature effects should be examined further to assess their relative importance in obtaining representative SO_3 samples.

2. Further consideration should be given to the effectiveness of sorption solutions in removing trace elements and the acidic and basic components from the gas stream. Also, what interference problems exist and how may they be overcome.

3. Cyclones were used to separate the particles into different size ranges. The larger cyclone in the flue-gas stream of our unit appeared to work properly (removing particulates >27 μ). The smaller cyclones in the Method 5 rigs produced somewhat of a problem in that they tended to plug after

several minutes of sampling. The small cyclones were heated to about 375 F which should reduce sticking tendencies in the particles. Nevertheless, the particles clung to the neck of the small cyclones making a clean-cut separation impossible. Enlarging the neck of the cyclone improved the separation but changed the size fraction range in the cyclone. Further consideration should be given to these cyclones if used in the Method 5 rig.

4. A further look at the effect on the sample of using cold traps to remove moisture, and pyrex wool filters to retain particles, would be worthwhile in the gas analysis part of the sampling.

5. The use of stainless steel tubing in sampling NO_2 should receive careful attention since heated stainless steel can reduce NO_2 to NO.

6. If time requirements for analysis is an important factor in the sampling and analyses program, the following should be considered (1) the actual time requirements needed to carry out a complete analysis of all samples regardless of other factors, and (2) the time required to have an analysis carried out taking into consideration other activities of the contractor's analytical laboratory. The latter area may lead to the need of analytical assistance from outside laboratories. The contractor should therefore have a clear understanding of the identity of such laboratories, the quality and reliability of their work, and the cost for analysis.

7. An item requiring serious consideration in a sampling and analysis program is the cost involved in carrying out the analyses (as well as the sampling) part of this program. Cost estimates should be made for each analysis carried out on each sample. This requires a detailed analysis plan such as shown in Table 4. Consideration of costs prior to sampling can be an important factor in determining the extent of sampling and/or analysis carried out in the program.

8. The Level 1, 2, and 3 approach to sampling and analysing a PBU unit was not entirely satisfactory for our program. It was felt that a combined Level 1-Level 2 approach would be more cost and information effective than strictly adhering to Level 1 sample and analysis procedure. This is especially true for certain group analyses where it would be better to obtain sufficient and proper samples to analyse for individual components in a group (e.g., SO_3 =, SO_4 = NO_3^- NH_3^+) than to analyse the group as a whole. Also it appeared well worthwhile to spend extra time obtaining samples of specific components, e.g., HCN, NH_3, etc., than to return later for these samples.

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APPENDIX A

FLUIDIZED-BED COMBUSTION SAMPLING AND ANALYSIS DATA REPORT - RUN NOS. 1, 2, AND 3

APPENDIX A

FLUIDIZED-BED COMBUSTION SAMPLING AND ANALYSIS DATA REPORT - RUN NOS. 1, 2, AND 3

This appendix presents the sampling and analysis data obtained from Run Nos. 1 and 2, carried out in January and April, 1976, respectively. Firing conditions and gaseous components measured in Run No. 3 are also included. It is the sole intent here to present the sampling and analysis data. It is not the intent of this report to analyze the results in terms of the overall fluidized-bed combustion process.

The purpose of this program was to develop comprehensive procedures for collecting and analyzing fluidized-bed combustion reactants and emission products. Battelle's 6-inch fluidized-bed combustion unit was used to carry out Run Nos. 1, 2, and 3 toward accomplishing the objective of this program.

Samples were collected and analyzed in accordance with the original (Run No. 1) and revised (Run No. 2) Fluidized-Bed Sampling Plan submitted to EPA. Figure A-1 shows the sampling locations used to obtain data for Run Nos. 1, 2, and 3. The sample identification numbers associated with each location are derived as follows. Each sample is given a three-digit number, e.g., 0-1-6-3, where the first digit represents the run number (here #1), the second digit gives the sample location (position 6 in the example), and the last digit is the sample number for that location (sample 3 at location 6 in the example).

Table A-1 in Run Nos. 1 and 2 gives a breakdown of the samples taken from each location and the analyses performed and is the key for identifying all samples taken in the runs. No significant amount of reduced sulfur compounds, b.P.<450 C, were found in the Run No. 1 samples. Therefore, no table on reduced sulfur compounds is given in Run No. 1 (see Table A-11 Run No. 2). Tables A-14 through A-19, Run No. 2, list the appropriate

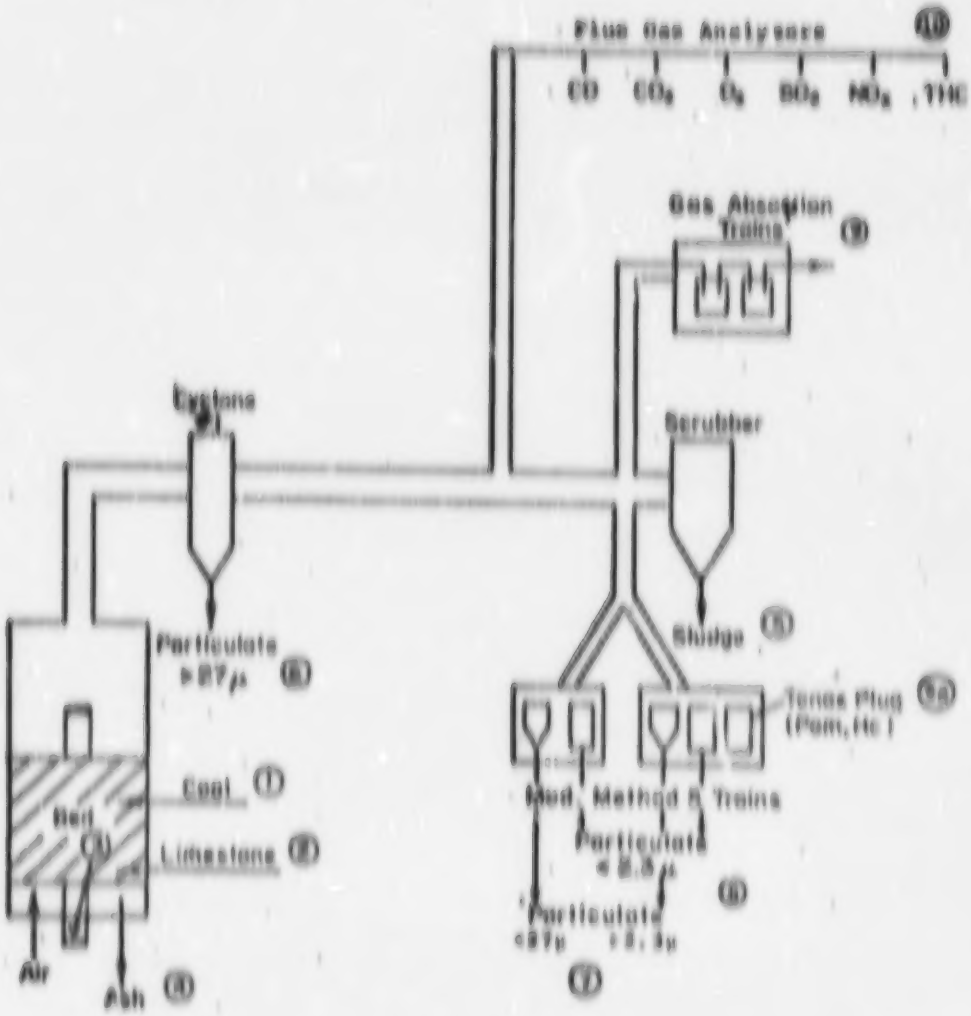

FIGURE A-1. SCHEMATIC OUTLINE OF FLUIDIZED BED COMBUSTOR AND SAMPLING LOCATIONS, RUN NO. 1

detection limits for the analysis procedures used in this program. The tables in general are self-explanatory. Noise measurement data are given in the following section. An estimated cost breakdown for groups of samples taken in Run No. 2 are given in Table A-18 at the end of data presentation.

Noise Measurements

Some acoustic measurements were made in the laboratory in which the Battelle's Multisolid Fluidized-Bed Combustor is located. This particular unit is very quiet; the support equipment makes more noise than the combustion bed itself.

The following table shows the sound pressure levels as a function of center frequency octave bands. These measurements were taken with the microphone inside the enclosure, one foot away from the bed.

Center Frequency Octave Bands sec -1	31.5	63	125	250	500	1000	2000	4000	8000	16000
Sound Pressure Flat Level, dB	73.5	64.5	68	68	66.5	66	61.5	58.5	56	50

The present OSHA requirements is to keep the A-weighted level* at 90 dBA or less for an 8-hour per day exposure. The measured levels were well below this level.

The sound pressure level at a distance of 3 ft away from the rotary feed pump was 78 dBA A-weighted, and 82 dB on the flat scale. The background noise was 68 dBA on A-weighted, and 79 dB on the flat side.

The acoustic radiation from this small model is not a valid indication of the noise generation potential of a full-scale model. However, it is quite possible that even in full-scale combustion beds, the support equipment will make more noise than the combustion bed itself.

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* An adjusted scale taking into account the response of the human ear at various frequencies; the A-weighted level (dBA) is always less than the flat level (dB) at a given frequency.

TABLE A-1. SAMPLE IDENTIFICATION AND ANALYSES, RUN NO. 1

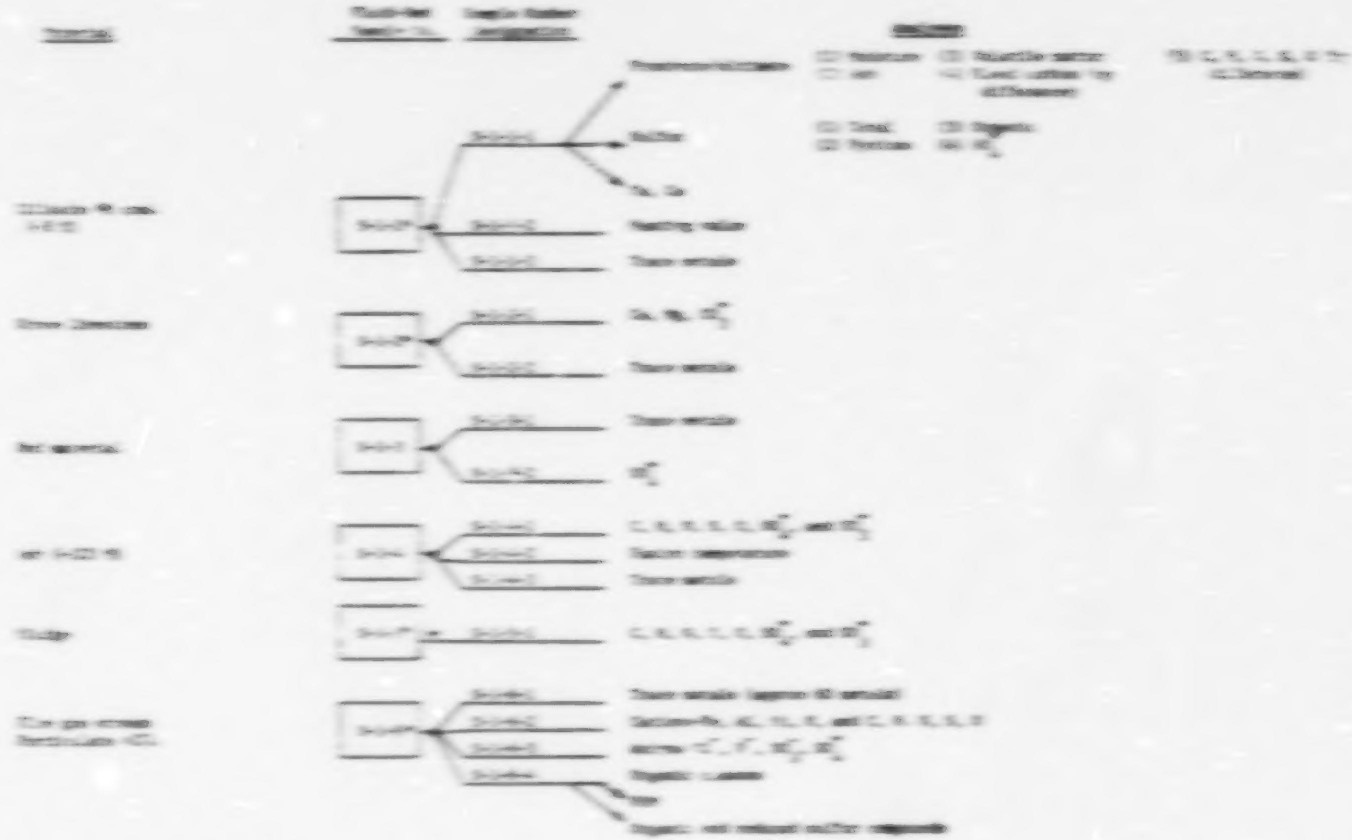

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TABLE A-2. SUMMARY OF RUN NO. 1 CONDITIONS

Run Number: BCL Number:	1A AL-2	1B AL-3	1C AL-4
Coal feed rate, lb/hr	15.3	16.9	15.2
Limestone feed rate, lb/hr	11.2	17.9	17.0
Air feed rate, lb/hr	139.9	144.4	150.6
Bed height: expanded, inches	48	48	48
settled, inches	11.8	13.3	11.8
Bed temperature, F	1560	1530	1525
Superficial gas velocity, ft/sec	8.9	9.0	9.4
Ca/S ratio	5/1	7.3/1	7.7/1
Particulate loading grams/m^3	NA	1.45	1.40

TABLE A-3. SIEVE ANALYSIS, RUN NO. 1

Illinois No. 6		Grove Limestone		Overflow Red Mater. 1	
Sieve No.	Wt. Percent	Sieve No.	Wt. Percent	Sieve No.	Wt. Percent
-8 + 16	28.0	-8 + 10	4.2	16	44.6
-16 + 20	17.4	-10 + 12	17.0	-16 + 20	33.8
-20 + 50	32.6	-12 + 16	37.7	-20 + 30	17.1
-50 + 100	9.7			-30 + 40	4.3
-100 + 200	4.9	-16 + 20	41.1	-40 + 50	0.07
-200 + 325	1.3	-20	0	-50 + 100	0.02
-325	6.1			-100	0.04

TABLE A-4. PROXIMATE/ULTIMATE ANALYSES OF FLUIDIZED-BED SAMPLES, RUN NO. 1

Material	Sample Number	Weight Percent													
		H_2O	ash	Volatile Matter	Fixed Carbon	C	H	N	S	O	Sulfur Total	Sulfur Pyritic	Sulfur Organic	Sulfur Sulfate	SO_2
Chlorite (B-coal)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—
Bed material	[illegible]													[illegible]	
Particulate (CO_2 1-100 mesh)	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]	[illegible]	[illegible]					[illegible]	[illegible]
Sludge	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]	[illegible]	[illegible]	[illegible]				[illegible]	[illegible]
Particulate (CO_2)	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]	[illegible]	[illegible]					[illegible]	
Particulate (CO_2)	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]	[illegible]	[illegible]					[illegible]	

TABLE A-1. METAL AND ANION ANALYSES OF FLUIDIZED-BED SAMPLES, RUN NO. 1

Material	Sample Number	Weight Percent										
		Na	Ca	Mg	CO_3	Fe	Al	Si	K	Cl	F	NO_3
Illinois #6 coal	9-1-1-1	0.23	0.41	0.38	0.68	—	—	—	—	—	—	—
Grove limestone	9-1-7-1		37.1	0.52	37.7							
Particulate $+CO_2$	9-1-6-2 and 9-1-6-3					5.42	2.53	6.80	0.47	0.12	0.023	0.008
Particulate $-CO_2$	9-1-7-2 and 9-1-7-3					6.60	7.36	11.0	2.10	0.40	0.019	0.003

TABLE A-6. ANALYSES OF ACIDIC AND BASIC GASES FROM FLUE GAS SAMPLES WITHDRAWN FROM STACK AT 348 F, RUN NO. 1

Component	Sample Number	Collection Method	mg/m^3	ppm
SO2	S-1-9-2	0.01N NaOH	62.9	43.5
HF	S-1-9-2	0.01N NaOH	0.065	0.082
NOX	S-1-9-3	1N KOH	0.077	0.070
NH_3	S-1-9-4	1N H_2SO_4	1.24	1.8
SO_3	S-1-9-5	Goksoyr-Ross	58.9	18.6

a See page 47, Recommendation (1).

TABLE A-7. TRACE ELEMENTS BY OPTICAL EMISSION SPECTROSCOPY SAMPLE NO. 8-1-9-5 (Collected in $KMnO_4$), RUN NO. 1

Component	ppmw[a]
Hg	--
Cd	<50
As	<50
Se	--
Te	--
Pb	<5
Sb	--

(a) All components were near or below minimum detection limit.

TABLE A-8. PAH ANALYSIS, RUN NO. 1

Component	NAS(1) Notation	Sample Weights, $\mu g/m^3$ Sample Number 8-1-8-1
Anthracene/Phenanthrene	-	57.3
Methyl Anthracenes	?	9.4
Fluoranthene	-	3.2
Pyrene	-	0.05
Methyl Pyrene/Fluoranthene	?	0.73
Benzo(c)phenanthrene	***	0.17
Chrysene/Benz(a)anthracene	*	0.37
Methyl Chrysenes	?	0.17
Benzo Fluoranthenes	**	
Benz(a)pyrene	***	
Benz(e)pyrene	-	
Perylene	-	
3-Methylcholanthrene	****	
Indeno(1,2,3,-cd)pyrene	*	
Benzo(ghi)perylene	-	
Dibenzo(a,h)anthracene	***	
Dibenzo(c,g)carbazole	***	
Dibenz(ai and ah)pyrenes	***	
Coronene	-	
Total		72.2

(1) Carcinogenicity rating as listed by National Academy of Sciences in "Particulate Polycyclic Organic Matter", 1972.

- \- Not carcinogenic.
- * Carcinogenic.
- **, ***, **** Strongly carcinogenic.
- ? Carcinogenicity not indicated by NAS.

TABLE A-9. ORGANIC CLASS ANALYSES
RUN NO. 1

Organic	Sample Weight µg/gram sample Sample No.	
	S-1-6-A	S-1-7-A
1	309	750
2	10.9	35
3	21.8	55
4	29.1	85
5	4.7	50
6	9.6	75
7	6.4	35
8	13.1	20

TABLE A-10. LEVEL 1 ANALYSES OF ORGANIC CLASSES, RUN NO. 1
(Refer to Table A-9 for total mass of each fraction)

Fraction	8-1-6-A	8-1-7-A
1	Vinyl unsaturated hydrocarbons	Aliphatic hydrocarbons, vinyl unsaturated hydrocarbons
2	Aliphatic esters	--
3	Aliphatic esters, ketone	Aliphatic esters
4	Phthalate ester	Conjugated ketone or quinone
5	--	Phthalate ester
6	--	--
7	--	--
8	--	--

TABLE A-11. ANALYSES OF GASEOUS COMPONENT IN FLUIDIZED-BED SAMPLES, RUN NO. 1

Sample Number	Component	Average Value
S-1-10-1	O_2, percent	6.5
S-1-10-2	CO_2, percent	14.3
S-1-10-3	CO, ppm	790
S-1-10-4	SO_2, ppm	700
S-1-10-5	NO_x, ppm	415
S-1-10-6	HC, ppmC	85

TABLE A-12. TRACE ELEMENT ANALYSIS OF FLUIDIZED-BED SAMPLES, RUN NO. 1, ppmw(a) (Except where designated percent)

Element	(Ill. #6 Coal) S-1-1-3	(Grove Lime-stone) S-1-2-2	(Bed Material) S-1-3-1	(Partic-ulate >27 μ <325) S-1-4-3	(Partic-ulate >37 μ) S-1-6-1	(Partic-ulate <27 μ) S-1-7-1
Li	0.13	2.9	5.7	220	NR	17
Be	0.17	<0.18	<0.18	18	2.6	6.0
B	93	6.2	33	710	500	>2000
F	110	140	170	290	290	450
Na	890	140	320	>3200	>1400	>0.55
Mg	400	>0.55	>0.55	>0.55	>0.55	>0.55
Al	>15	>3000	>3000	>15	>15	>15
Si	>15	>15	>0.55	>15	>15	>15
P	3.2	140	310	310	310	310
S	>0.55	240	>0.55	310	310	310
Cl	>1100	18	120	240	240	300
K	>1200	>0.55	>1600	>0.55	>0.55	>15
Ca	>4000	>15	>15	>15	>15	>15
Sc	1.6	<0.11	0.16	0.73	1.6	7.3
Ti	240	87	130	870	870	>2200
V	20	7	7	18	25	140
Cr	13	0.87	1.3	12	15	87
Mn	80	15	26	210	60	60
Fe	>15	>1200	>4600	>15	>15	>15
Co	4.0	0.14	0.14	14	2.1	14
Ni	13	0.69	23	46	23	99
Cu	9.0	2.2	78	18	16	120
Zn	17	4.0	17	80	67	140
Ga	1.7	0.23	1.1	2.3	2.3	11
Ge	2.0	--	1.4	1.0	1.0	14
As	2.7	<0.61	0.67	2.0	4.1	6.1
Se	0.29	--	--	4.4	0.94	9.4
Br	4.7	1.2	4.5	12	6.0	60
Rb	21	7.3	7.3	37	20	37
Sr	80	470	470	140	470	250
Y	9.4	1.7	1.6	8.1	1.6	29
Zr	10	7.0	28	15	13	120
Nb	1.1	0.32	0.69	1.2	1.2	16
Mo	2.9	0.67	1.2	1.1	1.1	14
Ag	--	--	--	0.10	--	0.10
Cd	0.10	--	0.14	0.67	0.67	1.0
Sn	0.28	0.12	0.55	0.92	1.2	12
Sb	0.56	--	--	0.67	0.67	1.4
Te	<0.17	--	--	--	--	--
I	0.10	2.9	0.29	1.2	0.58	29

TABLE A-12.

Element	(Ill. #6 Coal) S-1-1-3	(Grove Lime-stone) S-1-2-2	(Red Material) S-1-3-1	(Partic-ulate >37 μ <325) S-1-4-3	(Partic-ulate >37 μ) S-1-6-1	(Partic-ulate <37 μ) S-1-7-1
Ce	0.65	0.19	0.43	4.4	1.9	4.3
Ba	35	90	180	180	180	320
La	5.0	2.2	6.4	6.4	6.4	30
Ce	9.8	2.9	15	11	15	44
Pr	2.1	0.86	2.0	2.0	2.0	15
Nd	6.6	1.7	3.8	7.5	10	21
Sm	0.71	0.51	0.83	1.7	1.7	3.6
Eu	--	--	0.25	0.50	0.50	0.94
Gd	0.40	--	--	0.32	0.32	0.69
Tb	--	--	--	0.25	0.19	0.48
Dy	0.70	0.20	0.49	2.0	1.4	2.0
Ho	--	--	--	0.19	0.16	0.61
Er	0.34	--	0.11	0.28	0.28	0.56
Tm	--	--	--	--	--	0.14
Yb	0.23	<0.21	<0.49	1.6	1.6	2.5
Lu	--	<0.15	<0.15	0.38	0.50	0.50
Hf	0.18	1.8	1.1	0.79	1.8	1.8
Ta	0.27	0.33	0.87	0.43	0.87	0.87
W	0.31	<0.22	<0.32	0.36	<0.32	1.1
Hg	0.16	<0.01	<0.01	0.01	<0.01	14
Tl	0.59	--	--	1.0	0.48	10
Pb	0.47	0.86	1.9	7.2	4.1	21
Bi	--	<0.24	<0.24	<0.24	<0.24	0.80
Th	1.7	0.36	1.1	5.7	2.4	11
U	1.0	0.34	0.80	4.0	1.7	8.0

(a) Rhenium and Indium used as internal standards. Gold, Platinum, Iridium, Osmium, Iutecium, Thulium, Holmium, Palladium, Rhodium, Ruthenium present at less than 0.1 ppm/wt.

TABLE A-13. SAMPLE IDENTIFICATION AND ANALYSES, RUN NO. 7

TABLE A-13.

Material	Fluid-Bed Sample No.	Sample Number Designation	Analyses
Flue gas stream Particulate <[illegible]	SQ-7	S-2-7-1	Trace metals
		S-2-7-2	C, S, R, L, G
		S-2-7-3	Anions, Cl_2°, NO_2°, NO_3°, SO_4°, SO_3°
		S-2-7-4	Organic classes
		S-2-7-5	[illegible]
		Particle Size	Organic and reduced sulfur compounds
Flue gas stream Gases	SQ-9	(LG-2) S-2-9-1	Organic classes
			[illegible]
			Organics - reduced sulfur
		S-2-9-2 (LG-2)	HCl, HF
		S-2-9-3 (LG-2)	HCN
		S-2-9-4 (LG-2)	NH_3
		S-2-9-5 (LG-4)	Trace elements (solution)
		S-2-9-6 (LG-3)	SO_3 (Dekanyr-Base)
Gases, continuous monitoring	SQ-10	S-2-10-1	O_2
		S-2-10-2	CO_2
		S-2-10-3	CO
		S-2-10-4	SO_2
		S-2-10-5	NO_2
		S-2-10-6	HC

TABLE A-14. SUMMARY OF RUN NO. 2 CONDITIONS

Coal feed rate, lb/hr	8.8
Limestone feed rate, lb/hr	4.3
Air feed rate, lb/hr	87.3
Bed height: expanded, inches	48
settled, inches	21.6
Bed temperature, F	1655
Superficial gas velocity ft/sec	6.0
Ca/S ratio	2.9
Particulate loading g/m^3	1.64

TABLE A-15. SIEVE ANALYSIS, RUN NO. 2

Illinois Coal # 6		Limestone		Overflow Bed Material	
Sieve No.	Wt. %	Sieve No.	Wt. %	Sieve No.	Wt. %
+ 8	0.14	-8 + 12	32.53	20	71.10
-8 + 12	13.53	-12 + 16	34.26	-20 + 30	18.47
-12 + 16	18.61	-16 + 20	24.69	-30 + 40	7.47
-16 + 20	14.32	-20	8.51	-40 + 50	2.16
-20 + 30	12.91			-50 + 100	0.66
-30 + 50	17.92			-100 + 200	0.05
-50 + 100	9.28			-200	0.12
-100 + 200	5.14				
-200 + 325	5.42				
-325	2.32				

TABLE A-1A. PROXIMATE/ULTIMATE ANALYSES OF FLUIDIZED-BED SAMPLES, ICB NO. 2

Material	Sample No.	Weight Percent[a]												
		H2O	AH	Volatile Matter	Fixed Carbon	C	H	N	S	Total	SO_4^{2-}	Sulfate Pyrite	Sulfate Pyrite	Sulfate Inorganic
Illinois #6 coal	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]
Sludge	[illegible]	[illegible]	[illegible]	—	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—	—	[illegible]
Bartholomew LD_1	[illegible]	[illegible]	[illegible]	—	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—	—	[illegible]
Bartholomew LD_2	[illegible]	[illegible]	[illegible]	—	—	[illegible]	[illegible]	[illegible]	—	[illegible]	—	—	[illegible]	[illegible]

(a) Status in Table indicates as analysis made. Lower limit of detection for each component listed in Table is about 0.2 percent.
(b) AC values reported as sulfur.

TABLE A-17. METAL AND ANION ANALYSES OF FLUIDIZED-BED SAMPLES, RUN NO. 2

Material	Sample No.	Weight Percent								
		NO_3^-	NO_2^-	$SO_3^=$	$S^=$	$SO_4^{=(a)}$	$CO_3^=$	Na	Ca	Mg
Illinois #6 Coal	S-2-1-1	—	—	—	—	—	0.11	0.16	—	—
Limestone	S-2-2-1	<0.0003	<0.0003	—	—	—	57.6	—	37.6	0.96
Overflow bed material	S-2-3-2	0.0012	0.0007	0.04	<.01	20.2	—	—	—	—
Bed material exh., -325 mesh	S-2-4-1	0.012	0.0041	0.16	0.14	16.4	—	—	—	—
Particulate >27 μ	S-2-6-3	0.006	0.0008	0.31	—	3.57	6.43	—	—	—
Particulate <27 μ	S-2-7-3	0.002	0.0006	<0.1	—	5.36	5.97	—	—	—

(a) Divide sulfate values by 3 for use in Table A-16.

TABLE A-14. ANALYSES OF ACIDIC AND BASIC GASES FROM FLUE GAS SAMPLES WITHDRAWN FROM STACK AT 240 F, NOW NO. 2

Sample No.	Component	ng/m^3	ppm
5-2-9-2	HCl	55.3	37.3
5-2-9-3	HF	0.57	0.70
5-2-9-5	HCN	0.20	0.18
5-2-9-4	NH_3	4.87	7.05
5-2-9-6	SO_2*	0.46	0.16

* See page 47, Recommendation (1).

TABLE A-19. TRACE ELEMENT ANALYSES OF FLUIDIZED-BED SAMPLES BY ATOMIC ABSORPTION AND OPTICAL SPECTROSCOPY, RUN NO. 2

Sample No. 8-7-9-5

Component	ppmw	ng/m^3
Hg	0.007	9(a)
Cd	<0.04	<52
As	0.01	19
Se	<0.01	<19
Te	<0.2	<260
Be	<0.02	<26
Pb(b)	<1.0	<1300
Ba(b)	<1.0	<1300

(a) Near lower detection limit. May be some contribution from solvent.

(b) Determined by optical emission spectroscopy; all others by atomic absorption.

TABLE A-20. PAH ANALYSES, RUN NO. 2

Component	MAS(1) Notation	8-2-3-5	8-2-3-6	ng/m³ (a) 8-2-4-5	8-2-4-6	8-2-7-5	8-2-8-4
Anthracene/phenanthrene	c	<8	18.55	470	<4	810	2067
Methyl anthracenes	?			30.8		73.8	581
Fluoranthene	c			511		551	1504
Pyrene	c			91.9		36.8	611
Methyl pyrene/fluoranthene	?			20.4		14.1	38.1
Benzo(c)phenanthrene	***			15.3		18.4	14.0
Chrysene/benz(a)anthracene	*			81.7		73.9	35.1
Methyl chrysenes	?			20.4		11.0	3.5
7,12-Dimethylbenz(a)anthracene	****			<0.1		<0.7	<0.4
Benzo fluoranthenes	**			51.0		38.9	8.8
Benzo(a)pyrene	***						
Benzo(e)pyrene	c			35.9		30.8	3.5
Perylene	c			3.0		<0.7	<0.4
Methylbenzopyrenes	?			10.2		7.4	1.8
3-Methylcholanthrene	****			<0.1		<0.7	<0.4
Indeno(1,2,3,-cd)pyrene	*			7.0		7.4	3.5
Benzo(ghi)perylene	c			8.0		7.0	3.5
Dibenzo(a,h)anthracene	***			<0.1		<0.7	<0.4
Dibenzo(a,c)anthracene	***			<0.1		<0.7	<0.4
Dibenz(a) and chrysenes	***			<0.1		<0.7	<0.4
Coronene	c			<0.1		<0.7	<0.4
Minimum Detection Limit(b)		4	0.04	0.1	4	0.7	0.4

(a) Use the following conversion factors to convert from ng/m³ to ng/gram sample (solid sample only; i.e., M-2-8-1 not included)

Sample No:	8-2-3-5	8-2-3-6	8-2-4-5	8-2-4-6	8-2-7-5
Multiply values by:	0.021	11.7	1.47	0.06	0.53

(b) Detection limits vary with sampling conditions encountered, i.e., in accordance with amount of sample collected and gas volume analyzed. For extra samples the average detection limit in units of ng/gram sample is about 0.21.

(c) Carcinogenicity ratings as listed by National Academy of Sciences in "Particulate Polycyclic Organic Matter", 1972:

* Mod. (carcinogenic)
** Strong (carcinogenic)
***, etc. Some (strongly carcinogenic), ?
? Activity rating not indicated by NAS.

TABLE A-21. ORGANIC CLASS ANALYSES, RUN NO. 2

Organic Class	$\mu g/m^3$ [a]					
	B-2-3-4	B-2-4-4	B-2-5-3	B-2-6-4	B-2-7-4	B-2-9-1
1	1288	11.5	247	372	144	4158
2	41	2.5	231	422	83.2	605
3	275	6.3	214	144	150	2364
4	170	5.6	184	112	118	1873
5	135	1.0	91.9	73.8	70.7	610
6	181	2.3	150	66.8	141	919
7	181	7.2	124	162	536	1033
8	52.7	3.3	28.7	38.7	8.1	10.9

(a) Multiplication factors given in Table A-20 can be used here to convert from ug/m^3 to ug/gram sample (solid samples only).

TABLE A-22. LEVEL 1 ANALYSES OF ORGANIC CLASSES, RUN NO. 2
(Refer to Table A-21 for total mass of each fraction)

Sample 2-3-4

Cut 1 - Aliphatic hydrocarbon containing a significant amount of vinyl unsaturation.

Cut 2 through 6 - Contain only traces of hydrocarbon structure. Quantity of material is very low.

Cut 7 - Material concentration extremely low. A trace of aliphatic and carbonyl structure is present.

Sample 2-4-4

Cut 1 - Aliphatic hydrocarbon containing a small amount of unsaturation including vinyl.

Cut 2 - Aliphatic hydrocarbon containing a small amount of carbonyl.

Cut 3 - Aliphatic hydrocarbon containing some aliphatic ester.

Cut 4 - Carboxylic acid ester plus aliphatic ether groups, possibly a vinyl ether.

Cut 5 - A small amount of phthalate ester.

Cut 6 - Nil

Cut 7 - Primarily aliphatic - 2 different carbonyls are present, one of which is probably a ketone.

Sample 2-5-1

Cut 1 - Aliphatic and fused ring aromatic hydrocarbons; pyrene and benzpyrene types are possible.

Cut 2 - Similar to 1 but concentration of fused ring aromatics is higher.

Cut 3 - Some of the fused ring aromatics of cuts #1 and #2 but primarily an aromatic ketone. Nitrile* groups are present. A small amount of hydroxyl structure is present.

Cut 4 - Aromatic ketone and quinone structures. Small amounts of nitrile* and hydroxyl.

Cut 5 - Aromatic ketone and quinone structures. A trace of nitrile. A small amount of anhydride or other strained ring carbonyl is probable.

Cut 6 - A complex mixture of many types of carbonyl, aliphatic, aromatic structures and with a trace of nitrile*.

Cut 7 - Same as Cut 6.

Cut 8 - Only a trace of material; complex carbonyl structures.

TABLE A-22. (Continued)

Sample 2-6-4

Cut 1 - Aliphatic hydrocarbons.

Cut 2 - Ester (very small amount of material).

Cut 3 - Trace of ester plus other carbonyl.

Cut 4 - Trace of material containing several carbonyls.

Cut 5 - Trace of material containing carbonyl.

Cut 6 - Trace of material containing carbonyl.

Cut 7 - Trace of material containing carbonyl.

Cut 8 - Nil

Sample 2-7-4

Cut 1 - Aliphatic and fused ring aromatics plus silicone.

Cut 2 - Aliphatic and fused ring aromatics plus a small amount of ester.

Cut 3 - A mixture of aliphatic and aromatic esters plus a trace of nitrile[a].

Cut 4 - Ester, ketone, and quinone are probable; both aromatic and aliphatic structure are present.

Cut 5 - Aliphatic ester, probably unsaturated.

Cut 6 - Aromatic strained ring or halogenated carbonyl.

TABLE A-23. REDUCED ORGANIC SULFUR ANALYSES, RUN NO. 2

Component	Sample No.	Sample Wt. Gram	Reduced Organic Sulfur Compounds, µg[a] With Retention Time of Benzothiophene	Reduced Organic Sulfur Compounds, µg[a] With Retention Time of Dibenzothiophene	Miscellaneous	Remarks
Overflow bed material	[illegible]	[illegible]	None	None	None	No reduced organic sulfur compounds found in [illegible] or [illegible] above 5 µg. About one dozen nonsulfur compounds. Major portion in C_{14} to C_{22} range; 25 to 500 µg quantities.
-[illegible] mesh overflow bed material	[illegible]	[illegible]	–	–	–	
Particulate [illegible]	[illegible]	[illegible]	25	5		50 µg naphthalene
Particulate [illegible]	[illegible]	[illegible]	None	5	2 cpds at 5 µg each	20 to 40 µg nonsulfur cpd's in C_{10} to C_{16} range
Tonus	[illegible]	—	1500	[illegible]	8 cpd's at 20 to 100 µg each	2 non-sulfur compounds at levels of about [illegible] µg and 15 at 200 to 1200 µg
Sludge	[illegible]	[illegible]	40	200	1 cpd—100 µg	About 20 nonsulfur compounds at levels of 50 to 300 µg

(a) µg of material found in total sample weight given in Column 3. Minimum detection limit is about 0.5 µg for the above samples.

TABLE A-24. ANALYSES OF GASEOUS COMPONENTS IN FLUIDIZED-BED SAMPLES, RUN NO. 2

Component	Average Value
O_2, percent	3.6
CO_2, percent	17.3
CO, ppm	2090
SO_2, ppm	730
NO_x, ppm	350
HC, ppm C	380

TABLE A-25. TRACE ELEMENT ANALYSIS OF FLUIDIZED-BED COMBUSTION SAMPLES, RUN NO. 2, ppmw (except where designated percent)

Element	Ill. #6 Coal S-2-1-3	Grove Lime-stone S-2-2-2	Bed Material S-2-3-1	-325M Bed Material S-2-4-3	Sludge S-2-5-2	Partic-ulate >27μ S-2-6-1	Partic-ulate <27μ S-2-7-1
Li	20	3	1	10	10	10	20
Be	2	<0.005	<0.005	0.5	0.2	0.2	2
B	<0.03	1	5	30	50	50	300
F	≤3	≤10	≤3	≤10	≤5	≤5	≤20
Na	~2%	200	200	~1%	3000	3000	5000
Mg	~2%	~1%	2000	~2%	5000	5000	~1%
Al	~5%	~0.1%	~0.1%	~1%	~3%	~5%	~5%
Si	~20%	~1%	~0.5	~8%	~30%	~30%	~20%
P	100	10	20	50	50	50	200
S	5000	50	3000	~2%	1000	1000	3000
Cl	~0.5%	50	50	~1%	200	800	~1%
K	~0.6%	~0.3%	~0.2%	~2%	~5%	~1%	~2%
Ca	5000	~30%	~30%	~30%	~7%	~7%	~7%
Sc	3	1	1	10	30	30	30
Ti	5000	2	2	100	5000	1000	~1%
V	500	10	10	100	500	500	1000
Cr	100	5	10	100	100	100	100
Mn	100	100	20	1000	200	200	500
Fe	~5%	~0.02005%	~0.1%	~1%	~5%	~2%	~2%
Co	10	0.3	0.3	5	5	10	10
Ni	<10	<2	<2	50	200	200	100
Cu	30	3	3	2000	50	50	50
Zn	<10	<3	<3	30	<3	<3	<3
Ga(a)	<5	<0.5	<0.5	<5	<10	<5	<10
Ge	100	<0.2	10	10	20	3	10
As	<3	<0.5	1	10	3	1	3
Se (a)	<5	<1	<2	<5	<5	<5	<5
Br	10	0.5	1	20	1	0.5	1
Rb	20	5	5	20	10	5	10
Sr	500	500	500	300	500	200	300
Y	30	0.5	3	30	200	50	200
Zr	300	3	20	200	1000	200	200
Nb	3	0.3	0.5	5	20	3	5
Mo	30	<3	<3	30	10	20	10
Ru	<1	<1	<1	<1	<1	<0.5	<0.5
Rh	<0.5	<0.3	<0.3	<2	<0.5	<0.2	<0.5
Pd	<3	<2	<2	<2	<2	<2	<2
Ag (a)	<3	<1	<2	<5	<2	<1	<1
Cd	<30	<3	<10	<10	<3	<3	<3
In (a)	<10	<3	<2	<3	<1	<1	<1

TABLE A-25.

Element	Ill. #6 Coal S-2-1-2	Grove Lime-stone S-2-2-2	Red Material S-2-3-1	-125M Red Material S-2-4-1	Sludge S-2-5-2	Partic-ulate 37 S-2-6-1	Partic-ulate 37 S-2-7-1
Sn	<1	<1	<1	300	100	<2	10
Sb	<0.5	<0.1	<0.2	2	1	0.2	1
Te	<1	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
I	3	1	0.5	3	1	0.5	5
Cs	3	<0.5	0.3	5	3	0.5	2
Ba	200	100	200	300	5000	500	300
La	20	2	3	20	200	50	30
Ce	50	2	5	50	500	50	20
Pr	5	0.3	0.3	5	20	5	5
Nd	<10	0.5	0.5	5	50	20	20
Sm	<1	<0.3	<0.5	5	30	5	3
Eu	<0.5	<0.3	<0.3	2	10	1	1
Gd	<1	<0.3	<0.3	5	20	1	3
Tb	<0.2	<0.3	<0.1	0.5	2	0.5	0.3
Dy	<1	<0.2	<0.2	2	10	3	2
Ho	<0.3	<0.05	<0.05	0.5	3	0.5	0.5
Er	<0.5	<0.2	<0.2	2	5	0.5	1
Tm	<0.3	<0.05	<0.1	0.5	1	0.3	0.1
Yb	<0.5	<0.2	<0.2	0.2	5	1	1
Lu	<0.3	<0.05	<0.05	<0.1	0.5	<0.1	<0.1
Hf	<2	<0.5	<0.5	1	10	2	<0.5
Ta	<0.5	<0.3	<0.5	<0.3	<1	<0.2	<0.2
W	<1	<0.3	<0.5	1	2	0.3	<0.5
Re	<1	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Os	<1	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Ir	<1	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Pt	<1	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
Au	<0.5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Hg	<2	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
Tl	<1	<0.1	<0.2	5	10	5	10
Pb	<1	3	1	300	200	20	100
Bi	<0.5	<0.5	<0.1	1	10	<0.1	1
Th	<1	<0.2	0.2	10	30	5	5
U	<0.3	<0.5	0.5	5	30	2	2

(a) Memory from previous sample.

TABLE A-26. APPROXIMATE DETECTION LIMITS FOR SAMPLES RUN ON SPARK SOURCE MASS SPECTROMETER, RUN NO. 2 (refer to Table A-25)

Element	MDL[a] (PPMW)	Element	MDL (PPMW)	Element	MDL (PPMW)
Li	0.005	Y	0.3	Hf	0.3
Be	0.005	Zn	0.3	Ta	0.2
B	0.03	Nb	0.3	W	0.3
F	0.5	Mo	0.3	Re	0.2
Na	0.1	Ru	0.3	Os	0.2
Mg	3.0	Rh	0.3	Ir	0.2
Al	10.0	Pd	0.3	Pt	0.3
Si	2.0	Ag	1.0	Au	0.1
P	0.3	Cd	3.0	Hg	0.3
S	0.5	In	1.0	Tl	0.1
Cl	0.5	Sn	1.0	Pb	0.2
K	0.5	Sb	0.1	Bi	0.1
Ca	0.5	Te	0.3	Th	0.1
Sc	0.3	I	0.3	U	0.1
Ti	0.3	Cs	0.3		
V	0.3	Ba	0.5		
Cr	0.3	La	0.3		
Mn	0.3	Ce	0.5		
Fe	0.3	Pr	0.2		
Co	0.3	Nd	0.5		
Ni	2.0	Sm	0.3		
Cu	0.3	Eu	0.3		
Zn	1.0	Gd	0.3		
Ga	0.3	Tb	0.1		
Ge	0.2	Dy	0.2		
As	0.3	Ho	0.05		
Se	1.0	Er	0.2		
Br	0.3	Tm	0.05		
Rb	0.3	Yb	0.2		
Sr	0.3	Lu	0.05		

[a] Minimum detection limit for samples of approximate composition studied in program.

TABLE A-27. DETECTION LIMITS FOR METALS ANALYSIS BY ATOMIC ABSORPTION, RUN NO. 3 (refer to Table A-1.)

Element	MDL(a) ppm	MDL(a) (ng/m^3)
Hg	0.005	6.5
Cd	0.04	52
As	0.01	13
Se	0.03	39
Te	0.2	260
Be	0.02	26
Pb(b)	1.0	1300
Ba(b)	1.0	1300

(a) Minimum Detection Limit for samples of approximate composition analyzed in this study

(b) Determined by Optical Emission Spectroscopy.

TABLE A-28. DETECTION LIMITS FOR ACID AND BASIC GASES, RUN NO. 2 (refer to Table A-18)

Solution Analysis		
Compound	Method of Analysis	MDL, ppm[a]
HCl	Ion Chromatograph	0.06
HF	Ion Chromatograph	0.06
HCN	Ion Selective Electrode	0.01
NH_3	Ion Selective Electrode	0.01
$SO_4^=$	Ion Chromatograph	0.01

(a) Minimum Detection Limits for samples collected in this program.

TABLE A-29. DETECTION LIMITS FOR ANIONS AND METALS, [illegible] NO. 2 (Solid Sample, refer to Table A-17)

Compound	Analysis Method	MDL (Wt. Percent)
$CO_3^=$	Titration	0.05
NO_3^-	Colorimetric	(0.005)
NO_2^-	Colorimetric	(0.005)
$SO_4^=$	Gravimetric	0.05
$SO_3^=$	Titration	0.05
$S^=$	"	0.01
Ca	Atomic absorption	.01
Mg	" "	.01
Na	" "	.01

TABLE A-10. SAMPLES FROM RUN NO. 2 AND ESTIMATED COST PER ANALYSIS

Analysis	Run No. 2 Sample Number	Estimated Cost, 1976
Particle size		$ 400
	S-2-1-4	
	S-2-2-1	
	S-2-3-1	
	S-2-4-1	
	S-2-7-1	
	S-2-8-1	
Trace elements		1600
Minor elements		1600
	S-2-1-3	
	S-2-2-2	
	S-2-3-1	
	S-2-4-3	
	S-2-5-2	
	S-2-6-1	
	S-2-7-1	
	S-2-8-1	
Organic classes/PONA/ organic sulfur		4040
	S-2-3-4	
	S-2-4-4	
	S-2-5-3	
	S-2-6-4	
	S-2-7-4	
	S-2-8-1	
CHNSO		750
	S-2-1-1	
	S-2-3-1	
	S-2-4-2	
	S-2-7-2	
	S-2-8-2	
Anions		
(a) NO_2^-, NO_3^-, F^-, NO_2^-, and NO_3^-		440
	S-2-3-2	
	S-2-5-1	
(b) NO_2^-, NO_3^-, F^-, NO_2^-, and NO_3^-		440
	S-2-6-3	
	S-2-7-3	
	S-2-8-3	

TABLE A-30.

Analysis	Run No. 2 Sample Number	Estimated Cost, 1976
(c) $SO_4^=$, $SO_3^=$	S-2-3-1	$ 120
(d) NO_2^-, NO_3^-, $CO_3^=$	S-2-2-1	150
SO_3	S-2-3-6	60
Elemental Analysis (AA)		
(a) Hg, Cd, As, Pb, Se, Te, Be	S-2-9-5	620
(b) Ca, Mg	S-2-2-1	120
(c) Na, Ca	S-2-1-1	120
Proximate	S-2-1-1	90
Sulfur (total, pyritic, organic, and sulfate)	S-2-1-1	180

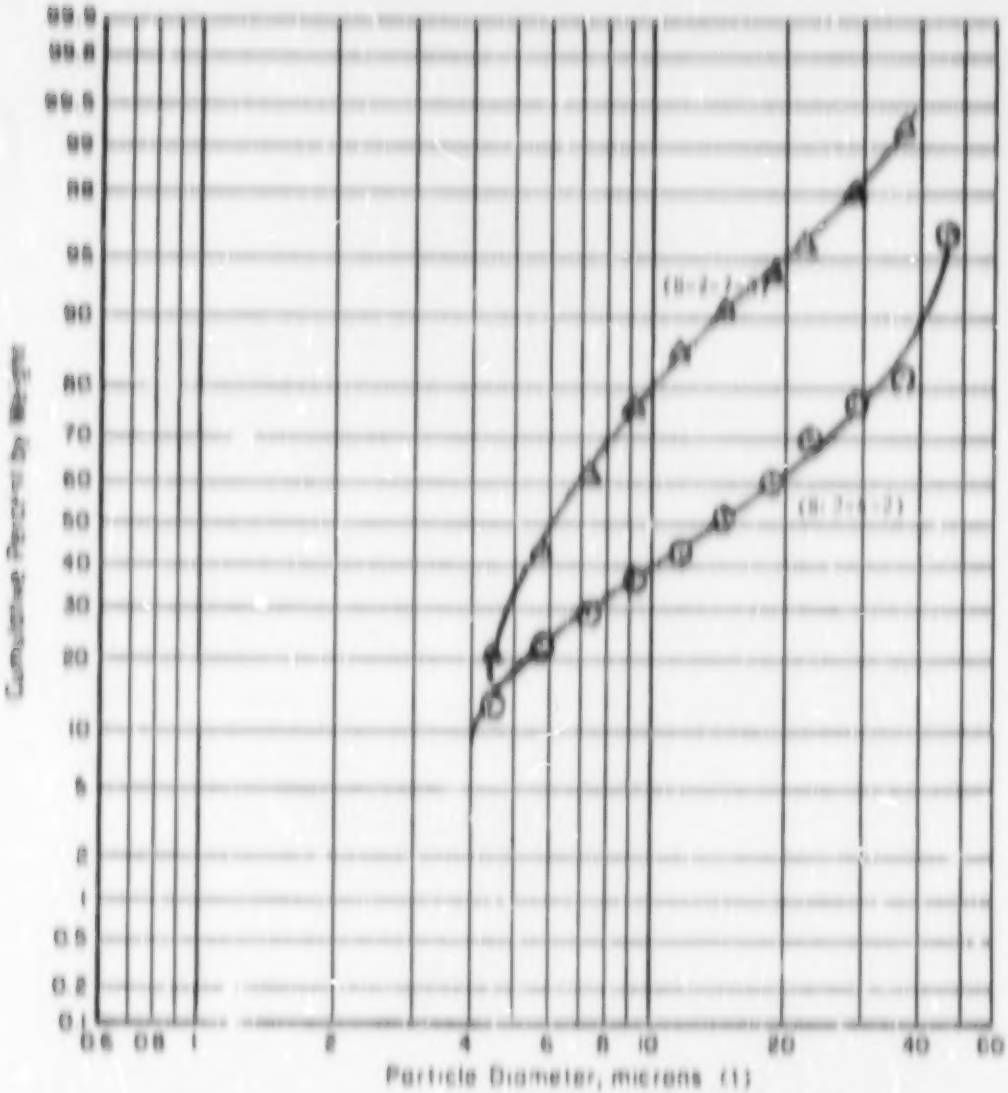

FIGURE A-2. PARTICLE SIZE ANALYSIS, RUN NO. 2
(B-2-6-2 Overflow Bed Material -325M
B-2-7-3 Particulate (27 μ, Method 5 Sig)

(1) Aerodynamic size, i.e., equivalent spherical particles of unit density.

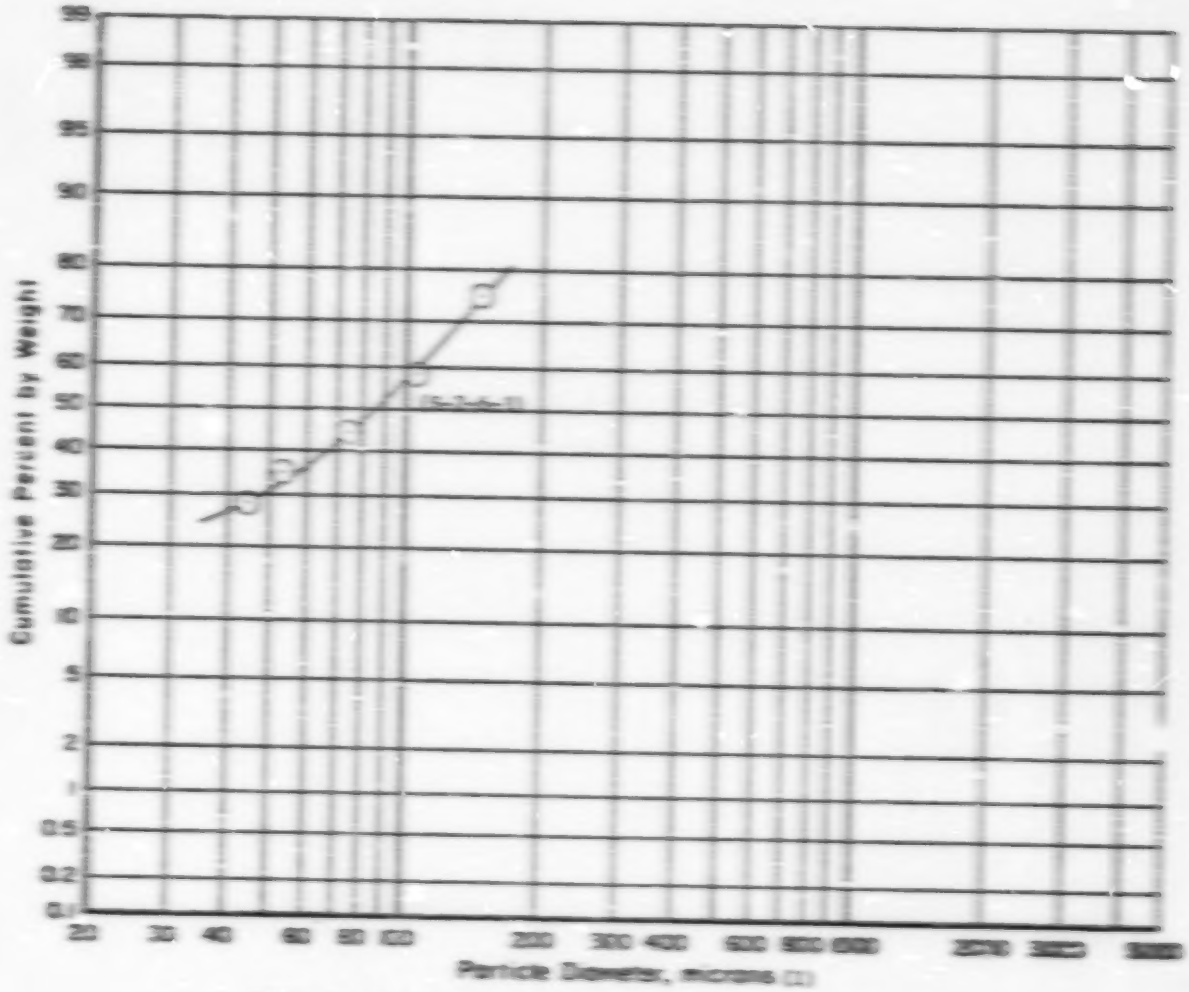

FIGURE A-3. PARTICLE SIZE ANALYSIS, RUN NO. 2
(5-2-6-3 Particulate +27 μ, Cyclone No. 1

(1) Aerodynamic size, i.e., equivalent spherical particles of unit density.

TABLE A-31: SUMMARY OF RUN NO. 3 CONDITIONS

Coal feed rate, lb/hr		9.2
Limestone feed rate, lb/hr		8.1
Air feed rate, lb/hr		84.2
Bed height:	expanded, inches	48.0
	settled, inches	21.6
Bed temperature, F		1490.0
Superficial gas velocity, ft/sec		5.3
Ca/S ratio		7.1

TABLE A-32. SIEVE ANALYSIS, RUN NO. 1

Illinois No. 6 Coal		Limestone		Overflow Bed Material			
				Run AL8		Run AL9	
Sieve No.	Wt. %	Sieve No.	Wt. %	Sieve No.	Wt. %	Sieve No.	Wt. %
+8	0.14	-8 + 12	12.53	20	76.80	20	77.68
-8 + 12	13.93	-12 + 16	34.26	-20 + 30	13.96	-20 + 30	14.90
-12 + 16	18.61	-16 + 20	24.69	-30 + 40	5.21	-30 + 40	4.85
-16 + 20	14.32	-20	8.51	-40 + 50	2.30	-40 + 50	1.79
-20 + 30	12.91			-50 + 100	1.49	-50 + 100	0.72
-30 + 50	17.92			-100 + 200	0.12	-100 + 200	0.03
-50 + 100	9.28			-200	0.07	-200	0.03
-100 + 200	5.14						
-200 + 325	5.42						
-325	2.32						

TABLE A-13: ANALYSES OF GASEOUS COMPONENTS IN FLUIDIZED-BED SAMPLES, RUN NO. 1

Component	Average Value
O_2, percent	3.3
CO_2, percent	18.3
CO, ppm	4790.0
SO_2, ppm	620.0
NO_x, ppm	300.0
HC, ppm C	900.0